INTERNATIONAL POLYMER AND COLLOIDS GROUP
Spring 2019 NEWSLETTER

Secretary:
Prof. Michael Cunningham

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See you soon!

IPCG 2019 Conference
Sentosa Island, Singapore

IPCG 2019
June 23rd – 28th

Chair: Dr. Pauline Pei Li
Vice Chair: Dr. Bernd Reck
Local Organization: Dr. Alex van Herk

https://ipcg.info/ipcg-conf-2019

UPCOMING SHORT COURSES & CONFERENCES

International Latex Conference
Akron, Ohio, United States
August 6-7, 2019

Conference Chairman Jim Finn, President of Akron Dispersions

Advances in Emulsion Polymerization and Latex Technology
Davos Resort, Switzerland
August 19-23, 2019

Dr. Mohamed S. El-Aasser, Course Organizer
Professor, Department of Chemical & Biomolecular Engineering
Lehigh University

Dr. F. Joseph Schork, Course Organizer
Professor Emeritus, School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

News Items

Congratulations to Patrick Lacroix-Desmazes!

Patrick Lacroix-Desmazes of the Department of Molecular and Macromolecular Chemistry, CNRS-UM-ENSCM has been named Distinguished Member of the Chemical Society of France for the year 2018.

The title of "Distinguished Member" is awarded to a researcher, an industrialist or a teacher, a member of the SCF aged 45 and over, who has demonstrated excellence in the field of chemistry and has contributed to its expansion. This prize also aims to recognize and honor chemists who are particularly involved in the chemistry community.

The nomination of Patrick Lacroix-Desmazes was made in May during an official ceremony where all of the new Distinguished Members of the Year were honored.

Congratulations to Michael Cunningham!

Michael Cunningham along with his colleagues Pascale Champagne, Philip Jessop, and Warren Mabee were awarded the Brockhouse Canada Prize for Interdisciplinary Research in Science and Engineering, which recognizes outstanding Canadian teams of researchers from different disciplines who came together to engage in research drawing on their combined knowledge and skills, and produced a record of excellent achievements in the natural sciences and engineering in the last six years.

Find out more here.

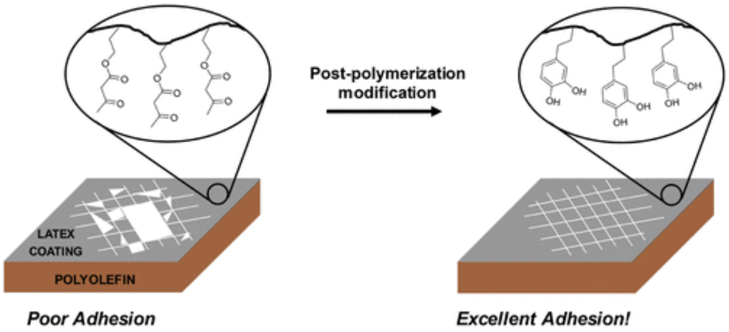
MEMBER CONTRIBUTIONS

Contribution: Matthew Carter

Matthew Carter, PhD
Senior Chemist
Core R&D, Formulation Science
The Dow Chemical Company

Catechol-Functionalized Latex Polymers Display Improved Adhesion to Low-Surface-Energy Thermoplastic Polyolefin Substrates

We report the synthesis and characterization of catechol-functionalized film-forming latexes that display excellent adhesion to low-surface-energy polyolefin-based substrates. The aromatic 1,2-diol functional group in catechol derivatives is believed to be responsible for enhancing the adhesion of a variety of polymers to a range of substrates. Here, we describe a postpolymerization modification approach to the design of emulsion polymers with catechol-functionalized side chains. A series of analogous small-molecule reactions, together with latex characterization by infrared (IR) spectroscopy and liquid chromatography (LC) methods, provides evidence for polymer functionalization. Films prepared from catechol-containing latexes displayed remarkable adhesion to challenging, commercially-available thermoplastic polyolefin (TPO) (as determined by a standard ASTM cross-hatch method). We provide evidence that covalent bonding and the unique catechol structure are required to promote adhesion. The catechol-functionalized emulsion polymers reported here represent a new class of functional latex, and this postpolymerization modification approach will present further opportunities to improve, modulate, and control the adhesion of water-borne coatings to a variety of polyolefin-based substrates.



https://pubs.acs.org/doi/abs/10.1021/acsapm.9b00130

Contribution: Prof. Marc A. Dubé

Prof. Marc A. Dubé, University of Ottawa, Canada

Recent publications:

Cazotti, J.C. Fritz, A.T., Garcia-Valdez, O. Smeets, N.M.B., Dubé, M.A., Cunningham, M.F., Grafting from Starch Nanoparticles with Synthetic Polymers via Nitroxide-Mediated Polymerization, Macromol. Rapid Commun., *in press* 2019.

Zhang, Y., Cunningham, M.F., Smeets, N., Dubé, M.A., Increasing Starch Nanoparticle Content in Emulsion Polymer Latexes, Ind. Eng. Chem. Res., *in press* 2019

Cummings, S., Zhang, Y., Smeets, N., Cunningham, M.F., Dubé, M.A., On the Use of Starch in Emulsion Polymerizations, Processes, 7, 140 (40 pages), 2019.

Cummings, S., Trevino, E., Zhang, Y., Cunningham, M.F., Dubé, M.A., Incorporation of Modified Regenerated Starch Nanoparticles in Emulsion Polymer Latexes, Starch, 71, 1800192 (13 pages), 2019.

Gabriel, V.A., Dubé, M.A., Bulk Free-Radical Co- and Terpolymerization of n-Butyl Acrylate/2-Ethylhexyl Acrylate/Methyl Methacrylate, Macromol. React. Eng., 13, 1800057 (8 pages), 2019.

Dastjerdi, Z., Cranston, E.D., Fraschini, C., Berry, R., Dubé, M.A., Polymer Nanocomposites for Emulsion-Based Coatings and Adhesives, Macromol. React. Eng., 13, 1800050 (15 pages), 2019.

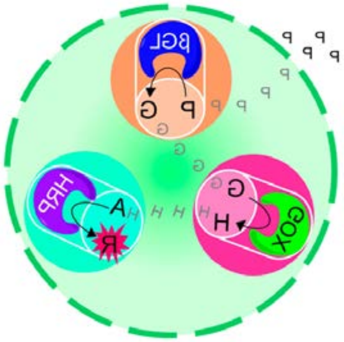
Ouzas, A., Niinivaara, E., Cranston, E.D., Dubé, M.A., Synthesis of Poly(Isobutyl Acrylate/n-Butyl Acrylate/Methyl Methacrylate) CNC Nanocomposites for Adhesive Applications via In Situ Semi-Batch Emulsion Polymerization, Polym. Comp., 40:1365-1377, 2019.

Contribution: Prof. Dr. Katharina Landfester

S.M. Jo, F.R. Wurm, K. Landfester
"Biomimetic Cascade Network between Interactive Multicompartments Organized by Enzyme-Loaded Silica Nanoreactors"
ACS Appl. Mater. Interf. **2018**, *10*, 34230-34237

Abstract:

Physical separation of reactions by interactive multicompartments in biological cells is an attractive motif to design efficient microreactors that create biomimetic cascade reactions. We present an aqueous compartment with three different subcompartments that comprise of silica nanoreactors with encapsulated enzymes, namely, β-glucosidase, glucose oxidase, and peroxidase, providing a model cascade reaction in confinement. The encapsulated enzymes retain their activity as the substrate can reach the active site and the silica shell further protects the enzymes from external stresses, such as heat and proteolytic degradation. We demonstrate the biomimetic cascade reaction in between the compartments ("organelles") inside of an additional microconfinement (water-in-oil emulsion). This strategy will allow us to design efficient multicompartmentalized reactors for further biological and organic reactions.

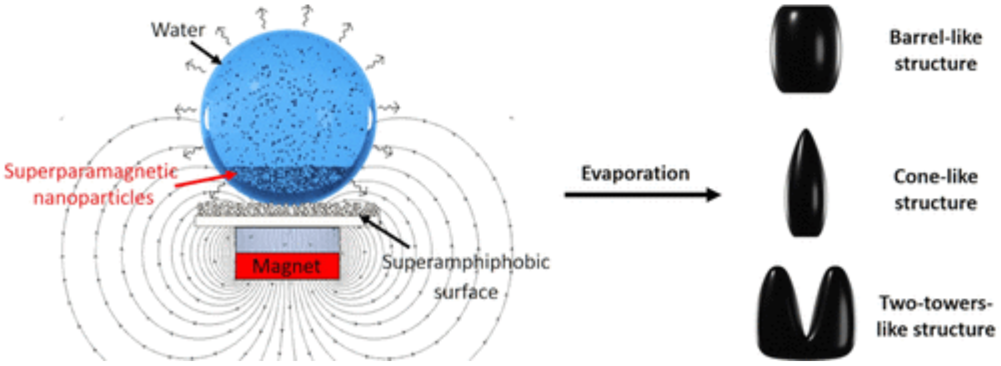


M. Hu, H.-J. Butt, K. Landfester, M.B. Bannwarth, S. Wooh, H. Therien-Aubin
"Shaping the Assembly of Superparamagnetic Nanoparticles"
ACS Nano **2019**, *13*, 3015-3022

Abstract:

Superparamagnetism exists only in nanocrystals, and to endow micro/macro-materials with superparamagnetism, superparamagnetic nanoparticles have to be assembled into complex materials. Most techniques currently used to produce such assemblies are inefficient in terms of time and material. Herein, we used evaporation-guided assembly to produce superparamagnetic supraparticles by drying ferrofluid droplets on a superamphiphobic substrate in the presence of an external magnetic field. By tuning the concentration of ferrofluid droplets and controlling the magnetic field, barrel-like, cone-like, and two-tower-like supraparticles were obtained. These assembled supraparticles preserved the superparamagnetism of the original nanoparticles. Moreover, other colloids can easily be integrated into the ferrofluid suspension to produce, by co-assembly, anisotropic binary supraparticles with additional functions. Additionally, the magnetic

and anisotropic nature of the resulting supraparticles was harnessed to prepare magnetically actuable microswimmers.



J. Reinholz, K. Landfester, V. Mailämder
"The challenges of oral drug delivery via nanocarriers"
Drug delivery 2018, 25, 1694-1705.

E. Rideau, R. Dimova, P. Schwille, F.R. Wurm, K. Landfester
"Liposomes and polymersomes: a comparative review towards cell mimicking"
Chem. Soc. Rev. **2018**, *47*, 8572-8610

S. Jiang, B.C. Ma, A. Kaltbeizel, G. Kizisavas, D. Crespy, K.A.I. Zhang, K. Landfester
"Visible light active nanofibrous membrane for antibacterial wound dressing"
Nanoscale Horizons **2018**, *3*, 439-446

D. Passlick, K. Piradashvili, D. Bamberger, M. Li, S. Jiang, D. Strand, P. Wich, K. Landfester, M. Bros, S. Grabbe, V. Mailänder
"Delivering all in one: Antigen-nanocapsule loaded with dual adjuvant yields superadditive effects by DC-directed T cell stimulation"
J. Contr. Release **2018**, *289*, 23-34

E. Rideau, F.R. Wurm, K. Landfester
*"*Giant polymersomes from non-assisted film hydration of phosphate-based block copolymers"
Polymer Chemistry **2018**, *9,* 5385-5394

J. Simon, J. Muller, A. Ghazaryan, S. Morsbach, V. Mailander, K. Landfester
"Protein denaturation caused by heat inactivation detrimentally affects biomolecular corona formation and cellular uptake"
Nanoscale **2018**, *10*, 21096-21105

J. Simon, S. Christmann, V. Mailänder, F.R. Wurm, K. Landfester
"Protein Corona Mediated Stealth Properties of Biocompatible Carbohydrate-based Nanocarriers"
Isr. J. Chem. **2018**, *58*, 1363-1372

K. Katta, D. Busko, K. Landfester, S. Baluschev, R. Munoz-Espi
“Inorganic Protection of Polymer Nanocapsules: A Strategy to Improve the Efficiency of Encapsulated Optically Active Molecules”
Isr. J. Chem. **2018**, *58*, 1363-1372

K. Katta, D. Busko, Y. Avlasevich, K. Landfester,S. Baluschev, R. Muñoz-Espí
“Ceria/polymer nanocontainers for high-performanceencapsulation of fluorophores”
Beilstein J. Nanotechnol. **2019**, *10*, 522–530.

L. Yang, L. Caire da Silva, H. Thérien-Aubin, M.B. Bannwarth, K. Landfester
“A Reversible Proton Generator with On/Off Thermoswitch”
Macromol. Rapid Commun. **2019**, *40*, Art. No. 1800713

S. Han, M. Raabe, L. Hodgson, J. Mantell, P. Verkade, T. Lasser, K. Landfester, T. Weil, I. Lieberwirth
“High-Contrast Imaging of Nanodiamonds in Cells by Energy Filtered and Correlative Light-Electron Microscopy: Toward a Quantitative Nanoparticle-Cell Analysis”
Nanoletters **2019**, *19*, 2178-2185

B. Iyisan, K. Landfester
“Modular Approach for the Design of Smart Polymeric Nanocapsules”
Macromol. Rapid Commun. **2019**, *40*, Art. No. 1800577

Contribution: Prof. Hideto Minami

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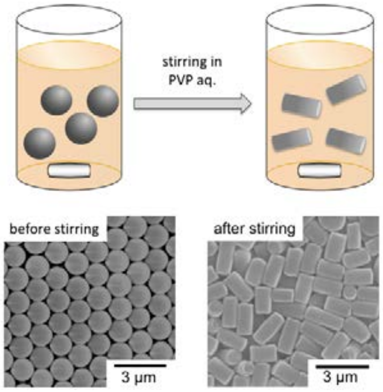
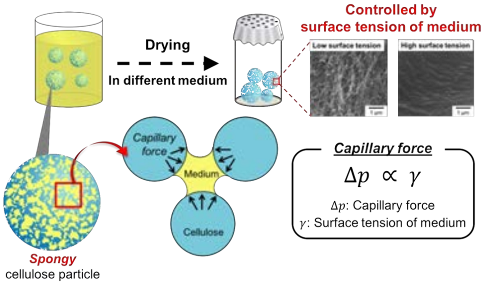
Recent Publications

・A Facile Method for Preparation of Polymer Particles Having a “Cylindrical” Shape, Li Wei, T. Suzuki, H. Minami, *Angew. Chem. Int. Ed.,* **57**, 9936 –9940 (2018)

A facile and novel approach to prepare monodisperse polystyrene (PS) particles having a “cylindrical” shape was discovered. The proposed synthetic method involved dispersion polymerization of the spherical PS particles stirred in a polyvinylpyrrolidone (PVP) aqueous solution for several hours using a magnetic stirrer at room temperature. In the presence of PVP, the spherical PS particles deformed into cylindrical shapes following stirring; however, the particles did not deform in the absence of PVP. The deformation rate of the particles was affected by the molecular weight of the dissolved PVP. This stirring method is not only highly efficient and provides high yield, but is also applicable to other materials such as polymethyl methacrylate. Moreover, the cylindrical particles were successfully applied as particulate surfactants in a Pickering emulsion system, which exhibited excellent stability as comparison with the system using spherical particles as a surfactant. In the latter case, the emulsion was left standing for more than 4 months.



・Morphology Control of Porous Cellulose Particles by Tuning the Surface Tensions of Media at Drying, T. Omura, K. Imagawa, T. Suzuki, H. Minami, *Langmuir,* **34,** 15490-15494 (2018)



Emulsion polymerization using bio-surfactant (sodium surfactin), which has a very low critical micelle concentration (CMC) (2.9×10^{-3} mmol/L) and biodegradability, was carried out and mechanism of the polymerization was investigated by comparing conventional surfactant (sodium dodecyl sulfate, SDS) system. The mechanism was likely to be divided into three different areas, which was sharp contrast to emulsion polymerization system using conventional surfactant. In low concentration of Surfactin (above CMC), the PS particles would be prepared under the mechanism of soap-free emulsion polymerization. On the other hand, in high concentration, PS particles should be prepared under emulsion polymerization mechanism, however, the slope (0.23) of $\log N_p$-$\log C_s$ (N_p; the number of particle, C_s;

concentration of Surfactin) did not obey to Smith-Ewart theory (0.6) which would be due to high adsorbability of Surfactin.

・Mesoporous magnetic silica particles modified with stimuli-responsive P(NIPAM-DMA) valve for controlled loading and release of biologically active molecules, M. Tanjim, M. A. Rahman, M. M. Rahman, H. Minami, S. M. Hoque, M. K. Sharafat, M. A. Gafur, H. Ahmad, *Soft Matter,* **14,** 5469-5479 (2018)

Mesoporous magnetic silica particles bearing a stimuli-responsive polymer valve were prepared and their performance as a microcapsule was evaluated. In this study, first, mesoporous magnetic iron oxide (Fe_3O_4) particles were prepared by a solvothermal method. Then, the magnetic particles were coated with silica and functionalized with vinyl groups using 3-(trimethoxysilyl)-propyl methacrylate (MPS). Subsequently, the Fe_3O_4/SiO_2 composite particles grafted with MPS were used to carry out the seeded precipitation copolymerization of *N*-isopropylacrylamide (NIPAM) and 2,2-dimethylaminoethyl methacrylate (DMA). Here *N*,*N′*-methylenebisacrylamide (MBA) was used as a cross-linker. Brunauer–Emmett–Teller (BET) surface analysis suggested that the mesoporous structure was retained in the final Fe_3O_4/SiO_2/P(NIPAM–DMA–MBA) composite hydrogel particles. The prepared Fe_3O_4/SiO_2/P(NIPAM–DMA–MBA) composite hydrogel microspheres exhibited a pH-dependent volume phase transition. At lower pH values (<7), the inclusion of DMA shifted the volume phase transition to higher temperature because of the protonation of the tertiary amine groups. The composite hydrogel particles possessed a high saturation magnetization (51 emu g^{-1}) and moved under the influence of an external magnetic field. The loading-release behaviour of these biologically active molecules suggested that a portion of the encapsulated guest molecules was released at a temperature below the lower critical solution temperature, LCST (<35 °C).

・Zwitterionic poly(2-(methacryloyloxy) ethyl phosphorylcholine) coated mesoporous silica particles and doping with magnetic nanoparticles, M. K. Debnath, M. A. Rahman, K. Tauer, H. Minami, M. M. Rahman, M. A. Gafur and H. Ahmad, *Colloids Surfaces A: Physicochem. Eng. Aspects,* **555**, 80-87 (2018)

・Single step modification of micrometer-sized polystyrene particles by electromagnetic polyaniline and sorption of chromium(VI) metal ions from water, M. K. Debnath, M. A. Rahman, H. Minami, M. M. Rahman, M. A. Alam, M. K. Sharafat, M. K. Hossain, H. Ahmad, *J. Appl. Polym. Sci.,* **136**, 47524 (2019)

・Polymerized ionic liquids as durable antistatic agents for polyether-based polyurethanes, A. Tsurumaki, T. Iwata, M. Tokuda, H. Minami, M. A. Navarra, H. Ohno, *Electrochimica Acta,* **308**, 115-120 (2019)

Contribution: Prof. Dr. Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

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Reporter Daniel Horak
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Recent publications

Antifouling microparticles to scavenge lipopolysaccharide from human blood plasma. Vorobii M., Kostina N., Rahimi K., Grama S., Pop-Georgievski O., Šturcová A., Horák D., Grottke O., Singh S., Rodriguez-Emmenegger C., *Biomacromolecules* 20, 959-968 (2019).

Abstract. Currently, one of the most promising treatments of lipopolysaccharides (LPS)-induced sepsis is based on hemofiltration. Nevertheless, proteins rapidly adsorbed on the artificial surface of membranes which leads to activation of coagulation impairing effective scavenging of the endotoxins. To overcome this challenge, we designed polymer-brush-coated microparticles displaying antifouling properties and functionalized them with polymyxin B (PMB) to specifically scavenge LPS the most common endotoxin. Poly[(*N*-(2-hydroxypropyl) methacrylamide)-*co*-(carboxybetaine methacrylamide)] brushes were grafted from poly(glycidyl methacrylate) microparticles using photoinduced single-electron transfer living radical polymerization (SET-LRP). Notably, only parts-per-millions of copper catalyst were necessary to achieve brushes able to repel adsorption of proteins from blood plasma. The open porosity of the particles, accessible to polymerization, enabled us to immobilize sufficient PMB to selectively scavenge LPS from blood plasma.

Keywords: lipopolysaccharide; scavenging; poly[(*N*-hydroxypropyl) methacrylamide); polymyxin B; glycidyl methacrylate; microspheress

Peroxidase-like activity of magnetic poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) particles. Zasońska B.A., Šálek P., Procházková J., Müllerová S., Svoboda J., Petrovský E., Proks V., Horák D., Šafařík I., *Sci. Rep.* 9, 1543 (2019).

Abstract. Poly(glycidyl methacrylate) (PGMA) is prone to modifications with different functional groups, magnetic fluids or direct coupling with biological molecules. The purpose of this research was to synthesize new magnetically responsive particles with peroxidase-like activity. Poly(glycidyl methacrylate-*co*-ethylene dimethacrylate)

[P(GMA-EDMA)] particles containing carboxyl groups were obtained by emulsifier-free emulsion polymerization and hydrolysis and oxidation of PGMA with $KMnO_4$, resulting in poly(carboxymethyl methacrylate-*co*-ethylene dimethacrylate) [P(CMMA-EDMA)] particles. Thionine (Th) was also attached to the particles [(P(CMMA-EDMA)-Th] via EDC/NHS chemistry to observe its effect on electron transfer during the oxidation reaction. Finally, the particles were coated with a nitric acid-stabilized ferrofluid in methanol. The resulting magnetic particles were characterized by several methods, including scanning and transmission electron microscopy, X-ray photoelectron spectroscopy, and vibrating sample magnetometry. The effect of EDMA on the P(CMMA-EDMA) particle size and size distribution was investigated; the particle size changed from 300 to 340 nm, and the particles were monodispersed with a saturation magnetization of 11 Am^2/kg. Finally, the effects of temperature and pH on the peroxidase-like activity of the magnetic P(CMMA-EDMA) and P(CMMA-EDMA)-Th particles were investigated. The particles, which exhibited a high activity at pH 4–6 and at ∼37 °C, represent a highly sensitive sensor component potentially useful in enzyme-based immunoassays.

Keywords: poly(glycidyl methacrylate); emulsion polymerization; magnetic; thionine; peroxidase-like

Biocompatibility assessment of up- and down-converting nanoparticles: Implications of interferences with *in vitro* assays. Pem B., González-Mancebo D., Moros M., Ocaña M., Becerro A.I., Pavičić I., Selmani A., Babič M., Horák D., Vinković Vrček I., *Methods and Applications in Fluorescence* 7, 014001 (2019).

Abstract. The safety assessment of nanoparticles (NPs) is crucial during their design and development for biomedicine. One of the prerequisite steps during this evaluation is in vitro testing that employs cell-based assays not always validated and well-adapted for NPs. Interferences with *in vitro* assays may arise due to the nano-related optical, oxidative, fluorescent, surface and catalytic properties of NPs. Thus, proper validation of each assay system has to be performed for each NP type. This study aimed to evaluate the applicability of the most common in vitro cytotoxicity assays for the safety assessment of up- and down-converting lanthanide-doped NPs. Conventional cell viability tests and fluorescence-based assays for oxidative stress response were selected to determine the biological effects of up- and down-converting NPs to human brain cells. Comparison with known silver and iron oxide NPs was made for verification purposes. Both the plate reader and flow cytometric measurements were examined. The obtained results indicated that both types of Ln-doped NPs interfered to a much lesser extent than metallic NPs. In addition, the great potential of both up- and down-converting NPs for biomedicine was manifested due to their biocompatibility and low toxicity.

Keywords: up-converting; down-converting; nanoparticles; cytotoxicity

Antioxidant polymer-modified maghemite nanoparticles. Patsula V., Moskvin M., Siow W.X., Konefal R., Ma Y.-H., Horák D., *J. Magn. Magn. Mater.* 473, 517–526 (2019).

Abstract. Natural antioxidants, such as epigallocatechin-3-gallate and related phenolic compounds from tea, enhance particle cell-interactions and cellular uptake. In this study, surface of superparamagnetic iron oxide nanoparticles prepared by co-precipitation of Fe chlorides was modified with silica, polyethylenimine, poly(ethylene glycol), and poly(L-lysine) to protect the iron oxide core from redox-reactions with phenols, enhance uptake by the cells, prevent the particle aggregation, or enable conjugation with several phenol-based antioxidants. To reveal the relation between the particle uptake and chemical structure of the phenolic antioxidants, five of them were selected, namely phenol, phloroglucinol, chlorogenic, gallic, and tannic acid. After incubation of the phenol-modified nanoparticles with U87MG human glioma cells, intracellular levels of the reactive oxygen species were reduced in a similar manner, as measured by flow cytometry. Colorimetric iron assay revealed a comparable level of cell-associated particles, which was mostly independent on the applied external magnetic field. The results suggest that the poly(L-lysine)-based coating is responsible for the antioxidant effects of the particles; the phenol- and poly(L-lysine)-coatings enable effective colloidal stability in aqueous media and enhance cellular internalization of the nanoparticles.

Keywords: nanoparticles; antioxidant; phenolic compounds; poly(L-lysine)

Combined antitumor effect of surface-modified superparamagnetic maghemite nanoparticles and a vitamin E derivative on experimental Walker-256 mammary gland carcinosarcoma. Zasońska B.A., Pustovyy V.I., Babinskiy A.V., Palyvoda O.M., Chekhun V.F., Todor I.N., Petrovsky E., Kuzmenko O.I., Horák D. *J. Magn. Magn. Mater.* 471, 381-387 (2019).

Abstract. In a search for efficient anti-tumor agent, silica-coated superparamagnetic nanoparticles were designed and used in combination with vitamin E derivative as a potential new tool for anticancer treatment. The particles were characterized by numerous techniques, such as transmission electron microscopy and dynamic light scattering to determine the particle morphology and size both in dry state and water, atomic absorption spectroscopy to analyze the iron content, Fourier-transform infrared spectroscopy to confirm the presence of the functional groups, and vibrating sample magnetometry to determine the magnetic properties and content of maghemite. The next aim was to assess effect of the nanoparticles on suppression of experimental mammary gland carcinosarcoma W-256. Strong antitumor effect was achieved only with combined application of γ-Fe_2O_3@SiO_2 and acetate derivative of α-tocopherol (Toc-6-Ac) resulting in 58% of tumor volume reduction. The results were compared with those obtained with poly(*N,N*-dimethylacrylamide)-coated iron oxide particles described earlier.

Keywords: superparamagnetic; nanoparticles; α-tocopherol; mammary gland carcinosarcoma

Effect of Fe_3O_4@SiO_2 nanoparticles on glutamate transport in the brain nerve terminals and its regulation by particle size. Patsula V., Borisova T., Kostiv U., Galkin M., Pastukhov A., Horák D., *Nanosci. Nanotechnol. Lett.* 11, 1-9 (2019).

Abstract. Monodispersed silica-coated magnetite nanoparticles (Fe_3O_4@SiO_2) with diameters of 11, 20, and 24 nm were synthesized by thermal decomposition, hydrolysis and condensation of tetramethyl orthosilicate. Substantial Fe_3O_4@SiO_2 particle size effects on glutamate transport in brain nerve terminals were observed. The balance between tonic release and uptake of glutamate affects the extracellular glutamate concentration and physiological synaptic neurotransmission. A smaller particle diameter (11 nm) resulted in a greater extracellular concentration and tonic release of L-[^{14}C]-glutamate in rat synaptosomes; however, lower L-[^{14}C]-glutamate uptake and synaptic vesicle acidification was observed with larger particles (20 and 24 nm). The neuromodulatory effect of the Fe_3O4@SiO_2 nanoparticles in synaptosomes was considerably increased by decreasing the particle diameter from 24 to 11 nm. The particle diameter was determined to be a critical parameter, and the manipulation of this parameter could be used to control the effect of the nanoparticles in biotechnological and medical applications..

Keywords: magnetic; nanoparticles; glutamate transport; synaptosome

Contribution: Prof. Dr. Andrew Lyon

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Recent Publications

1. Zhu, M. N., Lu, D. D., Wu, S. L., Lian, Q., Wang, W. K., Milani, A. H., Cui, Z. X., Nguyen, N. T., Chen, M., Lyon, L. A., Adlam, D. J., Freemont, A. J., Hoyland, J. A. & Saunders, B. R. Responsive Nanogel Probe for Ratiometric Fluorescent Sensing of pH and Strain in Hydrogels. *Acs Macro Letters* **6**, 1245-1250, doi:10.1021/acsmacrolett.7b00709 (2017)

In this study a new pH-responsive nanogel probe containing a complementary nonradiative resonance energy transfer (NRET) fluorophore pair is investigated and its ability to act as a versatile probe of network-related changes in three hydrogels demonstrated. Fluorescent sensing using NRET is a powerful method for studying relationships between Angstrom length-scale structure and macroscopic properties of soft matter. Unfortunately, inclusion of NRET fluorophores into such materials requires material-specific chemistry. Here, low concentrations of preformed nanogel probes were included into hydrogel hosts. Ratiometric photoluminescence (PL) data for the gels labeled with the nanogel probes enabled pH-triggered swelling and deswelling to be studied as well as Ca2+-triggered collapse and solute release. PL measurements during compression of a nanogel probe labeled nanocomposite gel demonstrated mechanochromic behavior and strain sensing. The new nanogel probes have excellent potential for investigating the internal structures of gels and provide a versatile ratiometric fluorescent platform for studying pH and strain.

2. Kodlekere, P. & Lyon, L. A. Microgel core/shell architectures as targeted agents for fibrinolysis. *Biomaterials Science* **6**, 2054-2058, doi:10.1039/c8bm00119g (2018)

We demonstrate the utility of microgel core/shell structures conjugated to fibrin-specific peptides as fibrinolytic agents. Poly(N-isopropylmethacrylamide) (pNIPMAm) based microgels conjugated to the peptide GPRPFPAC (GPRP) were observed to bring about fibrin clot erosion, merely through exploitation of the dynamic nature of the clots. These results suggest the potential utility of peptide-microgel hybrids in clot disruption and clotting modulation.

3. Welsch, N., Brown, A. C., Barker, T. H. & Lyon, L. A. Enhancing clot properties through fibrin-specific self-cross-linked PEG side-chain microgels. *Colloids and Surfaces B-Biointerfaces* **166**, 89-97, doi:10.1016/j.colsurfb.2018.03.003 (2018)

Excessive bleeding and resulting complications are a major cause of death in both trauma and surgical settings. Recently, there have been a number of investigations into the design of synthetic hemostatic agents with platelet-mimicking activity to effectively treat patients suffering from severe hemorrhage. We developed platelet-like particles from microgels composed of polymers carrying polyethylene glycol (PEG) side-chains and fibrin-targeting single domain variable fragment antibodies (PEG-PLPs). Comparable to natural platelets, PEG-PLPs were found to enhance the fibrin network formation in vitro through strong adhesion to the emerging fibrin clot and physical, non-covalent cross-linking of nascent fibrin fibers. Furthermore, the mechanical reinforcement of the fibrin mesh through the incorporation of particles into the network leads to a three-fold decrease of the overall clot permeability as compared to control clots. However, transport of biomolecules through the fibrin clots, such as peptides and larger proteins is not hindered by the presence of PEG-PLPs and the altered microstructure. Compared to control clots with an elastic modulus of 460+/-260 Pa, PEG-PLP-reinforced fibrin clots exhibit higher degrees of stiffness as demonstrated by the significantly increased average Youngis modulus of 1770+/+/- 720 Pa, as measured by AFM force spectroscopy. Furthermore, in vitro degradation studies with plasmin demonstrate that fibrin clots formed in presence of PEG-PLPs withstand hydrolysis for 24 h, indicating enhanced stabilization against exogenous fibrinolysis. The entire set of data suggests that the designed platelet-like particles have high potential for use as hemostatic agents in emergency medicine and surgical settings.

4. Islam, M. R., Tumbarello, M. & Lyon, L. A. Deswelling induced morphological changes in dual pH- and temperature-responsive ultra-low cross-linked poly(N-isopropyl acrylamide)-co-acrylic acid microgels. *Colloid*

and Polymer Science **297**, 667-676, doi:10.1007/s00396-019-04492-8 (2019)

Poly(N-isopropylacrylamide) microgels prepared without exogenous cross-linker are extremely soft as a result of their very low cross-linking density, with network connectivity arising only from the self-crosslinking of pNIPAm chains. As a result of this extreme softness, our group and others have taken interest in using these materials in a variety of bioengineering applications, while also pursuing studies of their fundamental properties. Here, we report deswelling triggered structural changes in poly(N-isopropylacrylamide-co-acrylic acid) (ULC10AAc) microgels prepared by precipitation polymerization. Dynamic light scattering suggests that the deswelling of these particles not only depends on the collapse of the pNIPAm chains but is also influenced by the ionization state of the acrylic acid moieties present in the copolymer. The ULC10AAc microgel behaves like a traditional cross-linked pNIPAm microgel at pH 3.5, showing a sharp decrease in the hydrodynamic diameter around the lower critical solution temperature (LCST) of pNIPAm. As the pH is increased to 4.5, we observe multiple transitions in the deswelling curve, suggesting inhomogeneity in the structure and/or composition of the microgels. At pH 6.5, the microgels cease to be thermoresponsive over the studied temperature range due to increased charge repulsion between the fully deprotonated AAc groups and an increase in gel osmotic pressure due to solvated counterion ingress. Atomic force microscopy images of particles deposited at different temperatures reveal a temperature-induced morphological change, with punctate structures forming inside microgels at pH 4.5 and 6.5 and temperature above the gel volume phase transition temperature (VPTT).

Contribution: Prof. Per. B. Zetterlund

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Recently published papers

Scalable Aqueous RAFT Photo Polymerization-Induced Self-Assembly of Acrylamides for Direct Synthesis of Polymer Nanoparticles for Potential Drug Delivery Applications, N. Zaquen, H. Zhu,A. N. M. N. B. P. H. J. Kadir, T. Junkers, P. B. Zetterlund, C. Boyer, *ACS Applied Polymer Materials* **accepted**.

Polymerization-Induced Self-Assembly based on ATRP in Supercritical Carbon Dioxide, A. Alzahrani, D. Zhou, R. P. Kuchel, P. B. Zetterlund, F. Aldabbagh, *Polym. Chem.* **accepted**.

Miniemulsion Polymerization using Graphene Oxide as Surfactant: In Situ Grafting of Polymer, Y. Cai, Y. Fadil, F. Jasinski, S. C. Thickett, V. Agarwal, P. B. Zetterlund, *Carbon* **accepted**.

Alcohol-based PISA in Batch and Flow: Exploring the Role of Photoinitiators, N. Zaquen, W. A. A. W. Azizi, J. Yeow, R. P. Kuchel, T. Junkers, P. B. Zetterlund, C. Boyer, *Polym. Chem.* **accepted**.

Polymerization of Cubosome and Hexosome Templates to Produce Complex Microparticle Shapes, H. Wang, P. B. Zetterlund, C. Boyer, P. T. Spicer, *J. Colloid Interface Science*, **accepted**.

Electrically Conductive Polymer/rGO Nanocomposite Films at Ambient Temperature via Miniemulsion Polymerization Using GO as Surfactant, Y. Fadil, V. Agarwal, F. Jasinski, S. C. Thickett, H. Minami, P. B. Zetterlund, *Nanoscale* **2019***, 11,* 6566 - 6570.

Nano-Engineered Multiblock Copolymer Nanoparticles via RAFT Emulsion Polymerization, T. R. Guimarães, M. Khan, I. C. Morrow, H. Minami, G. Moad, S. Perrier and P. B. Zetterlund, *Macromolecules*, **accepted**.

Rapid Oxygen Tolerant Aqueous RAFT Photopolymerization in Continuous Flow Reactors, N. Zaquen, A. M. N. B. P. H. A. Kadir, A. Iasa, N. Corrigan, T. Junkers, P. B. Zetterlund, C. Boyer, *Macromolecules* **2019**, *52*, 1609–1619.

Exploitation of Compartmentalization in RAFT Miniemulsion Polymerization to Increase the Degree of Livingness, M. Khan, T. R. Guimarães, D. Zhou, G. Moad, S. Perrier, P. B. Zetterlund, *J. Polym. Sci.; Part A: Polym. Chem.* **accepted**.

Interfacial Cross-Linking of Self-Assembled Triblock Copolymer Nanoparticles via Alkoxysilane Hydrolysis and Condensation, G. H. Teo, P. B. Zetterlund, S. C. Thickett, *J. Polym. Sci.; Part A: Polym. Chem.* **accepted**.

Large Hexosomes from Emulsion Droplets: Particle Shape and Mesostructure Control, H. Wang, P. B. Zetterlund, C. Boyer, B. J. Boyd, T. J. Atherton, P. T. Spicer, *Langmuir* **2018**, *34*, 13662–13671.

Polymerization-Induced Self-Assembly Under Compressed CO_2: Control of Morphology Using a CO_2-Responsive MacroRAFT Agent, D. Zhou, R. P. Kuchel, S. Dong, F. P. Lucien, S. Perrier, P. B. Zetterlund, *Macromol. Rapid Commun*. **2018**, 1800335.

Visible Light-Mediated Polymerization-Induced Self-Assembly using Continuous Flow Reactors, N. Zaquen, J. Yeow, T. Junkers, C. Boyer, P. B. Zetterlund, *Macromolecules* **2018**, *51*, 5165-5172.

Photopolymerization in Dispersed Systems, F. Jasinski, P. B. Zetterlund, A. M. Braun, A. Chemtob, *Prog. Polym. Sci.* **2018**, *84*, 47-88.

Pickering Miniemulsion Polymerization using Graphene Oxide: Effect of Addition of Conventional Surfactant, Y. Fadil, F. Jasinski, T. W. Guok, S. C. Thickett, H. Minami, P. B. Zetterlund, *Polym. Chem.* **2018**, *9*, 3368-3378.

Contribution: Dr. Patrick LACROIX-DESMAZES & Dr. Julien PINAUD

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Contribution to IPCG Newsletter

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Recently published or submitted articles and articles in preparation:

- *"Photolatent ring-opening metathesis polymerization in miniemulsion: a powerful approach to produce polynorbornene latexes"* L. Pichavant, P. Lacroix-Desmazes, A. Chemtob, J. Pinaud, V. Héroguez ***Polymer Chemistry*** **2018**, *9*, 5481-5498. http://dx.doi.org/10.1039/C8PY01011K

Abstract: The use of miniemulsion Ring-Opening Metathesis Polymerization (ROMP) to form polyunsaturated latexes is still a largely unexplored field. The main obstacle remains the preparation of a chemically-stable monomer/catalyst miniemulsion, which is generally jeopardized by the high reactivity of ROMP catalysts at ambient temperature. To overcome this drawback, a photo-latent ROMP catalytic system has been employed for the first time. Our approach starts with an N-heterocyclic carbene (NHC) photogenerating system (1,3-bis(mesityl)imidazolium tetraphenylborate/2-isopropylthioxanthone) which enables the in situ formation of an active NHC-derived Ru catalyst. The ability to initiate the ROMP in miniemulsion by a photoactive route depends on the absorption conditions of the initial formulation due to irradiation attenuation by scattering. In this article, the optimization of an aqueous norbornene miniemulsion in order to improve the irradiation penetration depth is presented in the first part. In the second part, the miniemulsion ROMP is investigated by using the NHC photogenerating system and two ruthenium complex pre-catalyst [RuX$_2$(*p*-cymene)] dimers (X = Cl or I). Stable PNb latexes with particle size in the range of 100 nm were obtained.

- *"Large-Pore Periodic Mesoporous Organosilicas as Advanced Bactericide Platforms"* A. Birault, E. Molina, G. Toquer, P. Lacroix-Desmazes, N. Marcotte, C. Carcel, M. Katouli, J.R. Bartlett, C. Gérardin, M. Wong Chi Man ***ACS Applied Bio Materials*** **2018**, *1(6),* 1787–1792. http://dx.doi.org/10.1021/acsabm.8b00474

Abstract: Despite the versatility of periodic mesoporous organosilicas (PMOs), the bactericide capacity of these hybrid platforms has seldom been explored. Herein, we describe the synthesis of large-pore phenylene-bridged PMOs, mesostructured by polyion complex (PIC) micelles (PICPMOs) incorporating an antibiotic, neomycin B. A key feature of this approach is that the bioactive molecules are directly encapsulated within the PICPMOs during their formation. The engineered PICPMOs exhibit a well-ordered hexagonal mesophase with a molecular-scale crystallinity and large mesopores (8 nm), which facilitates pH-triggered delivery of the drug. The results obtained with a pathogenic *Escherichia coli* strain clearly demonstrate the potential of such PICPMOs for antibacterial applications.

- *"Unconventional pathways for designing silica-supported Pt and Pd catalysts with hierarchical porosity",* A.F. Sierra-Salazar, A. Ayral, T. Chave, V. Hulea, S.I. Nikitenko, S. Abate, S. Perathoner, P. Lacroix-Desmazes, In *Studies in Surface Science and Catalysis*, S. Albonetti, A. Quadrelli, S. Perathoner (Eds), Elsevier B. V., (**2019**), Vol. 178 *"Horizons in Sustainable Industrial Chemistry and Catalysis"*, Chapter 18, 377-397. https://doi.org/10.1016/B978-0-444-64127-4.00018-5

Abstract: Catalysis as a pillar of green chemistry is called to improve the performance of current chemical processes and to develop new and sustainable processes and products. In order to tackle the current challenges in sustainable chemistry, catalyst rational design approaches are necessary. Such approaches require tailoring tools for the catalyst preparation, which should also be environmentally friendly. This chapter starts by presenting the importance of heterogeneous catalysis in the catalyst market, followed by the top rated challenges in sustainable chemistry. Subsequently, a brief review of the techniques for texture tailoring and catalyst functionalisation is presented, highlighting the high potential of hierarchical porous catalysts. Finally, a few innovative techniques for the preparation of silica-supported Pt and Pd catalysts with hierarchical porosity are described.

- *"Synthesis of Lamellar mesostructured Phenylene-Bridged Periodic Mesoporous Organosilicas (PMO) templated by PolyIon Complex (PIC) micelles"* A. Birault, E. Molina, C. Carcel, J. Bartlett, N. Marcotte, G. Toquer, P. Lacroix-Desmazes, C. Gerardin, M. Wong Chi Man, ***Journal of Sol-Gel Science and Technology*** **2019**, *89(1),* 189-195. http://dx.doi.org/10.1007/s10971-018-4667-1

Abstract: Periodic mesoporous organosilicas (PMOs), obtained by the surfactant-mediated hydrolysis-condensation of bridged organosilanes, combine versatile organic functionalities with advantages of a stable inorganic framework. Here, we introduce a novel synthesis of lamellar mesostructured phenylene-bridged PMOs templated by polyion complex (PIC) micelles (PICPMOs). The micelles assemble by electrostatic interactions between oppositely charged polyelectrolytes, with one being part of a double-hydrophilic block copolymer (DHBC), and the other being a polybase oligochitosan (OC). The PICPMO material was characterized by a range of techniques, including TEM, IR spectroscopy, SAXS, TGA and elemental analysis, which indicates that the material exhibits long-range ordering with an inter-lamellae distance of around 15 nm. Advantages of the synthetic approach developed, together with potential applications of the PICPOs, are discussed.

- *"Radical polymerization of biobased monomers in aqueous dispersed media"* S. Molina-Gutiérrez, V. Ladmiral, R. Bongiovanni, S. Caillol, P. Lacroix-Desmazes, ***Green Chemistry*** **2019**, Tutorial Review, *21*, 36-53. http://dx.doi.org/10.1039/C8GC02277A

Abstract: This review highlights the design and synthesis of biobased monomers from renewable resources for the preparation of latexes in aqueous dispersed media. Biobased polymers have been widely studied and are still a hot topic as environmental concerns and regulations require the use of green chemistry principles as guidelines for the synthesis of new polymer materials. Consideration should equally be given to green polymerization processes such as industrially relevant aqueous emulsion and suspension polymerizations. However, the synthesis and polymerization of biobased monomers through polymerization in aqueous dispersed media have not been sufficiently explored. Hence, constraints and opportunities arising from previous research work in this area will be presented focusing on aqueous (mini)emulsion and suspension polymerizations.

- *"pH-mediated control over the mesostructure of ordered mesoporous materials templated by polyion complex micelles"* E. Molina, M. Mathonnat, J. Richard, P. Lacroix-Desmazes, M. In, P. Dieudonné, T. Cacciaguerra, C. Gérardin, N. Marcotte ***Beilstein Journal of Nanotechnology*** **2019**, *10*, 144-156. http://dx.doi.org/10.3762/bjnano.10.14

Abstract: Ordered mesoporous silica materials were prepared under different pH conditions by using a silicon alkoxide as a silica source and polyion complex (PIC) micelles as the structure-directing agents. PIC micelles were formed by complexation between a weak polyacid-containing double-hydrophilic block copolymer, poly(ethylene oxide)-*b*-poly(acrylic acid) (PEO-*b*-PAA), and a weak polybase, oligochitosan-type polyamine. As both the micellization process and the rate of silica condensation are highly dependent on pH, the properties of silica mesostructures can be modulated by changing the pH of the reaction medium. Varying the materials synthesis pH from 4.5 to 7.9 led to 2D-hexagonal, wormlike or lamellar mesostructures, with a varying degree of order. The chemical composition of the as-synthesized hybrid organic/inorganic materials was also found to vary with pH. The structure variations were discussed based on the extent of electrostatic complexing bonds between acrylate and amino functions and on the silica condensation rate as a function of pH.

- *"Polynorbornene latex synthesis by UV-triggered Ring-Opening Metathesis Polymerization in miniemulsion"* L. Pichavant, P. Lacroix-Desmazes, A. Chemtob, J. Pinaud, V. Héroguez ***in preparation***

Abstract: In this contribution, an innovative route based on a novel photo-latent ROMP initiator has been explored to synthesize polynorbornene latex particles in miniemulsion with high yield. For that, an annular photo-reactor, giving the advantage to perform the polymerization under controlled atmosphere, was used. Several parameters (droplet size, irradiance, pre-catalyst structure) were studied in order to improve the monomer conversion profiles, which finally led to the production of latex with high norbornene conversion (higher than 90%). Particular attention was paid to the microstructure of the formed polymer and a correlation between microstructure and the initiation mechanism has been investigated

Work in progress:

Valentin HETIER (PhD student, supervisors: Annie PRADEL, Laurence COURTHEOUX and Patrick LACROIX-DESMAZES; Julien PINAUD also takes part in the project) (2016-2019): *Synthesis of double hydrophilic block copolymers, synthesis of hybrid colloids for catalytic applications.*

Samantha MOLINA-GUTIERREZ (PhD student, supervisors: Patrick LACROIX-DESMAZES, Sylvain CAILLOL, Roberta BONGIOVANNI) (2017-2020): *Synthesis of waterborne bio-based latexes and applications for coatings.*

Andrea RUIU (Postdoc, supervisors: Patrick LACROIX-DESMAZES, Julien PINAUD, Cécile BOUILHAC) (2018-2019): *Recovery of Precious Metals from Spent Catalysts by Supercritical* CO_2 *Extraction Assisted by Polymers.*

Shashikala INDHUDARA SWAMY (Post-doc, supervisors: Julien PINAUD, Patrick LACROIX-DESMAZES) (2018-2019): *PhotoBase Generators for Delayed Ring-Opening Polymerization in bulk and in aqueous dispersed media*.

Baptiste QUIENNE (PhD student, supervisors: Julien PINAUD, Sylvain CAILLOL) (2019-2022) *Hydrosoluble polyhydroxyurethanes (PHUs) as rheological modifiers.*

Contribution: Prof. Stan Slomkowski

Contribution to IPCG Newsletter
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Recently published papers

A. Karaszewska, I. Kamińska, A. Nejman, B. Gajdzicki, W. Fortuniak, J. Chojnowski, S. Slomkowski, P. Sowinski
Thermal-regulation of nonwoven fabrics by microcapsules of n-eicosane coated with a polysiloxane elastomer
Mater. Chem. Phys. 226 (2019) 204–213

W. Szymanski, S. Lipa, W. Fortuniak, J. Chojnowski, P. Pospiech, U. Mizerska, S. Slomkowski, A. Nyczyk-Malinowska, M. Hasik
Silicon oxycarbide (SiOC) ceramic microspheres – Structure and mechanical properties by nanoindentation studies
Ceramics Int. 45 (2019) 11946–11954

D. Mickiewicz, T. Basinska, M. Gosecka, M. Gadzinowski, S. Slomkowski
Colloidal liquid crystal type assemblies of spheroidal polystyrene core/polyglycidol-rich shell particles (P[S/PGL])
formed at the liquid-silicon-air interface by a directed dewetting process
Polym. Adv. Techn. https://doi.org/10.1002/pat.4604

Contribution: Prof. Dr. Walter Richtering

Contribution to the IPCG Newsletter *Spring 2019*

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2019

Exploring the colloid-to-polymer transition for ultra-low crosslinked microgels from three to two dimensions
A. Scotti, S. Bochenek, M. Brugnoni, M. A. Fernandez-Rodriguez, M. F. Schulte, J. E. Houston, A. P. H. Gelissen, I. I. Potemkin, L. Isa, and W. Richtering
Nature Communications 10, 1418 (2019).
DOI: 10.1038/s41467-019-09227-5

Amphiphilic Microgels Adsorbed at Oil-Water Interface as Mixers of Two Immiscible Liquids
R. A. Gumerov, S. A. Filippov, W. Richtering, A. Pich, I. I. Potemkin
Soft Matter, 15, 3978-3986, 2019
DOI:10.1039/C9SM00389D

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M. Karg, A. Pich, T. Hellweg, T. Hoare, L. A. Lyon, J. J. Crassous, D. Suzuki, R. A. Gumerov, S. Schneider, I. I. Potemkin, W. Richtering
Langmuir, 35, 6231-6255, 2019
DOI:10.1021/acs.langmuir.8b04304

Distribution of Ionizable Groups in Polyampholyte Microgels Controls Interactions with Captured Proteins: From Blockade and "Levitation" to Accelerated Release
W. Xu, A. A. Rudov, R. Schroeder, I. V. Portnov, W. Richtering, I. I. Potemkin, A. Pich
Biomacromolecules, 20(4), 1578-1591, 2019
DOI:10.1021/acs.biomac.8b01775

On the mechanism of payload release from liposomes bound to temperature-sensitive microgel particles
O. V. Ivashkov, T. M. Yakimova, E. G. Evtushenko, A. P. H. Gelissen, F. A. Plamper, W. Richtering, A. Yaroslavov
Colloids and Surfaces A: Physicochemical and Engineering Aspects, 570, 396-402, 2019
DOI:10.1016/j.colsurfa.2019.02.069

Direct Monitoring of Microgel Formation during Precipitation Polymerization of N-Isopropylacrylamide Using in Situ SANS
O. L. J. Virtanen, M. Kather, J. Meyer-Kirschner, A. Melle, A. Radulescu, J. Viell, A. Mitsos, A. Pich, W. Richtering
ACS Omega, 4(2), 3690-3699, 2019
DOI:10.1021/acsomega.8b03461

Synthesis and Structure of Deuterated Ultra-Low Cross-Linked poly(N-isopropylacrylamide) Microgels
M. Brugnoni, A. C. Nickel, L. C. Kröger, A. Scotti, A. Pich, K. Leonhard, W. Richtering
Polymer Chemistry, Advance Article, 2019
DOI:10.1039/C8PY01699B

Cargo shuttling by electrochemical switching of core-shell microgels obtained by a facile one-shot polymerization
O. Mergel, S. Schneider, R. Tiwari, P. T. Kühn, D. Keskin, M. C. A. Stuart, S. Schöttner, M. de Kanter, M. Noyong, T. Caumanns, J. Mayer, C. Janzen, U. Simon, M. Gallei, D. Wöll, P. van Rijn, F. A. Plamper
Chemical Science, 10(6), 1844-1856, 2019
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Tunable 2D Binary Colloidal Alloys for Soft Nanotemplating
M. A. Fernandez-Rodriguez, R. Elnathan, R. Ditcovski, F. Grillo, G. M. Conley, F. Timpu, A. Rauh, K. Geisel, T. Ellenbogen, R. Grange, F. Scheffold, M. Karg, W. Richtering, N. H. Voelcker, L. Isa
Nanoscale, 10(47), 22189-22195, 2018
DOI:10.1039/C8NR07059H

Microgel in a Pore: Intraparticle Segregation or Snail-like Behavior Caused by Collapse and Swelling
I. V. Portnov, M. Möller, W. Richtering, I. I. Potemkin
Macromolecules, 51(20), 8147-8155, 2018
DOI:10.1021/acs.macromol.8b01569

Nanoscopic visualization of cross-linking density in polymer networks with diarylethene photoswitches
E. Siemes, O. Nevskyi, D. Sysoiev, S. K. Turnhoff, A. Oppermann, T. Huhn, W. Richtering, D. Wöll
Angewandte Chemie International Edition, 57(38), 12280-12284, 2018
DOI:10.1002/anie.201807741

Contribution: Prof. Alex Routh

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Recently completed work

Mercedes Fernández-Serrano, Francisco Ríos, Francisco Caparrós, Alexander F. Routh and Mariam Alhaj Salih Ortega, *Calcium alginate as a novel sealing agent for colloidosomes. Study of stability and microencapsulation efficiency*

We report the preparation of colloidosomes formed with a poly (methyl methacrylate-co-butyl acrylate) latex nanoparticle shell, sealed using calcium alginate as a novel non-toxicity and biodegradable sealing agent, with the aim being to encapsulate enzymes in detergent formulations. The method proposed, with vegetable oil as the continuous phase, avoids the use of harmful organic solvents. Allura red dye has been used as a water soluble molecule in the core to analyse the influence of variables such as sodium alginate concentration, nanoparticle concentration and water and propylene glycol as dispersion media on the formation and dispersion of the capsules, as well as the sealing and release profiles of the dye. The colloidosomes have been examined using optical, confocal and scanning electron microscopies. Working with the highest sodium alginate concentration and latex nanoparticle volume the encapsulation efficiency is around 60%. Propylene glycol achieves a better dispersion of the capsules when compared with water.

Qian Sun, Jianfeng Chen and Alexander F. Routh, *Coated colloidosomes as novel drug delivery carriers*.

Aqueous core microcapsules with a polymeric shell can be readily made by a self-assembly process. After locking the shell in place the capsules are termed colloidosomes. These capsules have been used for a range of biological encapsulations and have the advantage of ease of production and the absence of harsh solvents and processing conditions. The capsules are leaky so a secondary inorganic shell can be placed around them and bio-specific targeting achieved through antigen coupling. Release has been achieved through dissolution of the shell or rupture via ultrasound. The future direction for clinical application of these capsules is discussed. They need to be miniturised down to around 100 nm in diameter and release mechanisms need to be optimized.

Recently published papers

Weiping Liu, Amanda Carr, Kevin Yager, Alexander F. Routh and Surita R. Bhatia, *"Sandwich" Structures in Binary Nanoparticle Films and Effect of Size Ratio on Stratification Behavior*, Journal of Colloid and Interface Science 538: 209-217 2019.

Ismael Lobato Guarnido, Alexander F. Routh, Mercedes Fernandez Serrano, Michael D. Mantle and Patricia Marr, *Formation and Application of Polystyrene Microcapsules with Ionic Liquid in the Core,* ACS Sustainable Chemistry & Engineering 7(2):1870-1874 2019.

Fanny Yuen, Matthew Watson, Robert Barker, Isabelle Grillo, Richard Heenan, Alan Tunnacliffe and Alexander F. Routh, *Preferential adsorption to air-water interfaces: a novel cryoprotective mechanism for LEA proteins*, Biochemical Journal 476:1121-1135 2019.

Contribution: Prof. Alexander Zaichenko

Prof. Alexander Zaichenko Lviv Polytechnic National University

Articles:

1. *O.Paiuk, N.Mitina, M.Slouf, E.Pavlova, N.Finiuk, N.Kinash, A.Karkhut, N.Manko, T.Gromovoy, O.Hevus,Y.Shermolovich, R.Stoika, A.Zaichenko*. Fluorine-containing block/branched polyamphiphiles forming bioinspired complexes with biopolymers //Colloids and Surfaces B: Biointerfaces – 2019 - 174 – p.393–400 https://doi.org/10.1016/j.colsurfb.2018.11.047

   Colloidal-chemical characteristics of block/branched cationic and non-ionic polyamphiphiles containing poly(fluorine-alkyl methacrylate) (poly(FMA)) block and their intermolecular complexes with biopolymers were studied. The dependences of their surface activity and micelle size on the length of hydrophobic and hydrophilic blocks, as well as the length of side fluorine-alkyl branches were established. Poly(FMA)-block-poly(DMAEMA) was used for formation of interpolyelectrolyte complexes with plasmid DNA (pDNA) via their electrostatic interaction. Novel non-viral polyplexes were tested as gene delivery systems for mammalian cells. The results of DLS, TEM and MALDI-ToF studies demonstrated disaggregation of lysozyme (LYZ) aggregates in the presence of poly(FMA)-block-poly(NVP) and formation of the polyamphiphile…LYS complex possessing antibacterial action.

2. *L.Kobylinska, I.Ivasechko, N.Skorokhyd, R.Panchuk, A.Riabtseva, N.Mitina, A. Zaichenko, R. Lesyk, B. Zimenkovsky, R. Stoika, S.G.Vari.* Enhanced Proapoptotic Effects of Water Dispersed Complexes of 4-Thiazolidinone-Based Chemotherapeutics with a PEG-Containing Polymeric Nanocarrier// Nanoscale research letters, -2019 – V.14(1) - P. 140 (16) https://doi.org/10.1186/s11671-019-2945-7

   Aim: To study whether water formulation of the complex of 4-thiazolidinone derivatives with a PEG-containing polymeric nanocarrier enhances their pro-apoptotic action towards rat glioma C6 cells. *Methods:* Mechanisms of antineoplastic effects of 4-thiazolidinone derivatives were investigated in vitro with rat glioma C6 cells. Cell nativity, cell cycling pattern, and Annexin V expression were evaluated and DNA damage was estimated by DNA comet analysis. A novel water-based formulation of 4-thiazolidinone derivatives complexed with a polymeric nanocarrier was utilized for enhancing pro-apoptotic action towards C6 cells. *Results:* The studied 4-thiazolidinone derivatives use apoptosis mechanisms for killing rat glioma C6 cells, as confirmed by FACS analysis of these cells in pre-G1 stage, the appearance of Annexin V positive C6 cells, and an increased number of DNA comets of higher classes. Complexation of the studied compounds with a PEG-containing polymeric nanocarrier significantly increased pro-apoptotic effects in rat glioma C6 cells measured by all methods mentioned above. *Conclusion:* Complexation of 4-thiazolidinone derivatives with a PEG-containing polymeric nanocarrier provided them with water solubility and enhanced pro-apoptotic effects in rat glioma C6 cells.

3. *L.Kobylinska, I.Patereha, N.Finiuk, N.Mitina, A.Riabtseva, I.Kotsyumbas, R. Stoika, A.Zaichenko, S.G. Vari.* Comb-like PEG-containing polymeric composition as low toxic drug nanocarrier//Cancer Nanotechnology - 2018 - V9(11) -p1-13. https://doi.org/10.1186/s12645-018-0045-5

   Background: Development of biocompatible multifunctional polymeric drug carriers is crucial in modern pharmaceutics aimed to create “smart” drugs. The high potential of the PEGylated comb-like polymeric nanocarrier (PNC) in delivering both traditional and experimental drugs to tumor cells in vitro and in vivo has been demonstrated previously. In the present study, we investigated the general toxicity of polyethylene glycol (PEG) processed with both covalent and non-covalent attachments of PEG to compose a comb-like polymer that behaves like a simple chain of n monomers decorated with swollen side chains. The PNC possesses properties of a water-soluble surfactant containing methyl-terminated PEG side branches in some monomer units attached covalently to the carbon chain backbone. *Results:* We have demonstrated that the synthesized PNC possesses weak toxic effects toward human leukemia cells (HL-60 and Jurkat lines), as well as toward hepatocellular (HepG2), colon (HCT116) and breast (MCF-7) tumor cell lines. Additionally, after a long period (20 days) of intraperitoneal administration, the PNC had no significant toxic effects in laboratory white mice (470 mg/kg body mass in 1 ml) and Wistar rats (440 mg/kg body mass in 10 ml). *Conclusion:* The developed PNC we studied can be qualified as a compound of grade 4 toxicity (low toxicity substance). The reduced toxicity of this PNC in combination with its improved bioavailability and previously detected capability to enhance cytotoxicity toward tumor cells in vitro and potential tumor treatment effects in vivo suggests its potential as a safe drug delivery platform for treating various diseases, especially cancer.

4. *L.Kobylinska, N.Skorohyd, O.Klyuchivska, N.Mitina, A Zaichenko., R.Lesyk, B.Zimenkovsky, R.Stoika.* Increased antitumor efficiency and reduced negative side effects in laboratory mice of 4-thiazolidinone derivatives in complexes with PEG-containing polymeric nanocarrier// Biopolym. Cell. – 2018 - 34(4) – p.313-328

http://dx.doi.org/10.7124/bc.000985

Aim. To study an anticancer activity and to measure cytological and enzymatic indicators of general toxicity of 4-thiazolidinone-based compounds (Les-3288, Les-3833) in the NK/Ly lymphoma grafted to BALB/C mice. *Methods.* BALB/C mice were implanted with the ascitic NK/Ly lymphoma and treated for 14 days with 4-thiazolidinone derivatives – Les-3833 (2.5 mg/kg of bodyweight), Les-3288 (5 mg/kg of bodyweight), a complex of Les-3833 with the polymeric nanocarrier Les-3833+PNC (2.5 mg/kg of bodyweight) in water, and doxorubicin (1 mg/kg of bodyweight) used as a positive control. The lymphoma development was monitored by measuring the amount of ascitic fluid in the treated mice. The effects of the applied compounds were checked after 35 days of tumor growth. *Results.* A distinct decrease in the amount of the ascite fluid with lymphoma cells was revealed in the treated mice, while a 1.5-fold increase of its amount was detected in the untreated mice of control group. The 4-thiazolidinone derivatives demonstrated much less toxicity, and erythrocytes count stayed normal after 21 days of animal treatment. The development of NK/Ly lymphoma led to an increase in the neutrophils number, while the applied anticancer compounds reduced it significantly. Les-3833 and Les-3288 did not affect the number of lymphocytes over the normal level. The activity of aspartate and alanine aminotransferases in blood serum was elevated on the 14 day of treatment, and returned to the normal level on the 21 day. *Conclusion.* Novel 4-thiazolidinones Les-3833 and Les-3288 are effective in the treatment of NK/Ly lymphoma grafted to BALB/C mice. These derivatives induced had limited negative side effects in the treated mice.

5. *O.L.Paiuk, N.Ye.Mitina, A.O.Riabtseva, V.M.Haramus, L.V.Dolynska, Z.Ya.Nadashkevych, A.S.Zaichenko,* Structure and colloidal-chemical characteristics of polymeric surface active substances based on polyethylene glycol-containing macromeres // Voprosy khimii i khimicheskoi tekhnologii - 2018 - N6 - p. 63-71

http://dx.doi.org/10.32434/0321-4095-2018-121-6-63-71

The synthesis of comb-like homo- and copolymers with terminal peroxide fragment was investigated by polymerization of polyethylene glycol (PEG)-containing macromeres in the presence of functional peroxide-containing chain transfer agent. The dependence of kinetic and material polymeric chains lengths on chain transfer agent concentration was stated as a result of its weakly inhibitory effect. The copolymerization rate constants of PEG-methacrylate (PEGMA) with dimethyl maleate (DMM) were determined. The parameters of microstructure of copolymers were calculated. It was found that DMM crumbles blocks with PEGMA units and the copolymeric microstructure approach to the alternate sequence at a certain content of DMM. The structures of copolymers were confirmed by the results of elemental and functional analyses and IR-spectroscopy. The dependences of solubility and colloidal-chemical properties of comb-like PEG-containing polymers on their microstructure were established. The explanation of the solubility dependences and colloidal-chemical properties of comb-like PEG-contained polymers via PEG side chains weak interaction was confirmed. It was shown that the fragmentation of blocks with PEG-macromere units in the consequence of PEGMA and DMM copolymerization is the reason for significant changes in colloidal-chemical properties

6. *O.L.Paiuk, N.Ye.Mitina, N.I.Kinash, A.B.Yakymovych, O.I.Hevus, A.S.Zaichenko* Comb-like polyethylene glycol containing oligomeric surfactants with reactive terminal

groups // Ukrainian Chemistry Journal – 2018 –V.84(10) – p.98-106
https://ucj.org.ua/index.php/journal/issue/view/9/10-2018

Novel functional oligomers combining terminal reactive peroxide or epoxide groups and side polyethylene glycol (PEG) chains were synthesized via developed in our lab method of controlled polymerization of PEG-containing methacrylate based macromers in the presence of cumene derivatives with peroxide or epoxide functionalities as chain transfer agents (telogens). Using such chain transfer agents provides controlling the lengths of kinetic and material chains during polymerization and as a result not only obtaining oligomers with tailored molecular weight and molecular weight distribution but also amount of the oligomer molecules containing terminal peroxide or epoxide groups. The general scheme of the polymerization in the presence of functional telogens was proposed and confirmed by kinetic, structural and functional studies. The relative constants of chain transfer to peroxy- or epoxy-containing telogens were determined and their values are 0.29 or 0.28, respectively. Functional compositions of synthesized oligomers containing terminal functional peroxide or epoxide fragments were confirmed by IR-spectroscopy, gas-liquid chromatography, elemental and functional analyzes. Comb-like telechelic oligomers are water soluble surfactants forming micelles were studied using solution surface tension and DLS techniques. The sizes of polymeric micelles depend on the length of macromolecular backbone. The availability of reactive terminal groups in molecules of telechelic oligomers opens easy and simple way for the synthesis of block-copolymers via radical polymerization initiated by MP fragment or addition reaction of epoxide group.

Contribution: Dr. José M. Asua and Dr. Jose R. Leiza

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Institute for Polymers Materials “**POLYMAT**” and Grupo de Ingeniería Química, Centro Joxe Mari Korta, University of the Basque Country, Avda.Tolosa, 72, E-20018 Donostia-San Sebastián, Spain

Reported by José M. Asua and Jose R. Leiza

April 2019

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapter

“WATERBORNE ACRYLIC/CEO2 NANOCOMPOSITES FOR UV BLOCKING CLEAR COATS”.
M. Aguirre, M. Paulis, J.R. Leiza
Ed. Sher Bahadan Khan. IntechOpen , London 2018. ISBN: 978-1-78985-024-6

CONTROL OF POLYMERIZATION PROCESSES
M. C.C. Pinto, F. W. Gomesa, J. R. Leiza, J. C. Pinto
IN BOOK: REFERENCE MODULE IN CHEMISTRY, MOLECULAR SCIENCES AND CHEMICAL ENGINEERING (ELSEVIER). https://doi.org/10.1016/B978-0-12-409547-2.13919-8

Articles

INSIGHTS INTO THE NETWORK STRUCTURE OF CROSS-LINKED POLYMERS SYNTHESIZED VIA MINIEMULSION NITROXIDE-MEDIATED RADICAL POLYMERIZATION
E. Mehravar, A. Agirre, N. Ballard, S. van Es, A. Arbe, J.R. Leiza, J.M. Asua
MACROMOLECULES, 51, 23, 9740-9748 (2018).

HIGH BIOBASED CONTENT LATEXES FOR DEVELOPMENT OF SUSTAINABLE PRESSURE SENSITIVE ADHESIVES
A. Badía, J. Movellan, M.J. Barandiaran, J.R. Leiza
IND. & ENG. CHEM. RES. 57, 43, 14509-14516 (2018).

DYNAMIC OPTIMIZATION OF A TWO-STAGE EMULSION POLYMERIZATION TO OBTAIN DESIRED PARTICLE MORPHOLOGIES
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NITROXIDE MEDIATED POLYMERIZATION OF METHACRYLATES: WHY DISPOLREG 007 WORKS WHERE OTHERS FAIL?
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A. Simula, N. Ballard, M. Aguirre, J.R. Leiza, S. van Es, J.M. Asua
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N. Ballard, A.D. Law, S.A.F. Bon
SOFT MATTER Soft Matter, 15, 1186-1199 (2019).

FLEXIBLE AROMATIC DISULFIDE MONOMERS FOR HIGH-PERFORMANCE SELF-HEALABLE LINEAR AND CROSS-LINKED POLY(URETHANE-UREA) COATINGS
S. Nevejans, N. Ballard, M. Fernandez, B. Reck, J.M. Asua
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SYNTHESIS OF MECHANICALLY STRONG WATERBORNE POLY(URETHANE-UREA)S CAPABLE OF SELF-HEALING AT ELEVATED TEMPERATURES
S. Nevejans, N. Ballard, I. Rivilla, M. Fernandez, A. Santamaria, B. Reck, J.M. Asua
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THE INFLUENCE OF PARTICLE MORPHOLOGY ON THE STRUCTURE AND MECHANICAL PROPERTIES OF FILMS CAST FROM HYBRID LATEXES
E. Limousin, N. Ballard, J.M. Asua
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SOFT CORE–HARD SHELL LATEX PARTICLES FOR MECHANICALLY STRONG VOC-FREE POLYMER FILMS *E. Limousin, N. Ballard, J.M. Asua*
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SYNTHESIS OF CELLULOSE NANOCRYSTAL ARMORED LATEX PARTICLES FOR MECHANICALLY STRONG NANOCOMPOSITE FILMS
E. Limousin, N. Ballard, J.M. Asua
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CORRELATING MICROSTRUCTURE AND PERFORMANCE OF PU/(METH)ACRYLIC HYBRIDS AS HARDWOOD FLOOR COATING
S. Mehravar, K.J. Roschmann, P. Uribe Arocha, B. Reck, A. Agirre, R. Tomovska, J.M. Asua, N. Ballard
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S. Mehravar, N. Ballard, R. Tomovska, J.M. Asua
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EXPERIMENTAL VALIDATION OF A MATHEMATICAL MODEL FOR THE EVOLUTION OF THE PARTICLE MORPHOLOGY OF WATERBORNE POLYMER-POLYMER HYBRIDS: PAVING THE WAY TO THE DESIGN AND IMPLEMENTATION OF OPTIMAL POLYMERIZATION STRATEGIEs
N. Rajabalinia, S. Hamzehlou, J.R. Leiza, J.M. Asua
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DYNAMIC OPTIMIZATION AND NON-LINEAR MODEL PREDICTIVE CONTROL TO ACHIEVE TARGETED PARTICLE MORPHOLOGIES
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I. Emaldi, S. Hamzehlou, E. Erkizia, J.S. Dolado, A. Etxeberria, J.R. Leiza
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HIGH-PERFORMANCE UV PROTECTIVE WATERBORNE POLYMER COATINGS BASED ON HYBRID GRAPHENE/CARBON NANOTUBE RADICALS SCAVENGING FILLER
M. Prosheva, M.A. Aboudzadeh, G.P. Leal, J. Blazhevska Gilev, R. Tomovska
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PS/PMMA- CDSE/ZNS QUANTUM DOTS HYBRID NANOFIBERS FOR VOCS SENSORS
A. De San Luis, Z. Aguirreurreta, L.M. Pardo, A. Pérez-Marquez, J. Maudes, N. Murillo, M. Paulis, J.R. Leiza
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COPOLYMERIZATION OF (METH)ACRYLATES WITH VINYL ARAOMATIC MACOMONOMERS: UNDERSTANDING THE MECHANISM OF RETARDATION ON THE KINETICS WITH ACRYLATES
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ADSORPTION OF CO_2 GAS ON GRAPHENE–POLYMER COMPOSITES
G. Magi Meconi, R. Tomovska, R. Zangi
JOURNAL OF CO_2 UTILIZATION 32, 92–105 (2019)

Accepted

ISOLATION OF THE INTERACTION BETWEEN $CACO_3$ FILLER AND ACRYLIC BINDER. PART I: EFFECT OF THE SURFACTANT AND FUNCTIONAL MONOMER TYPE
V. Álvarez, N. Williams, M. Paulis
PROG. ORG. COAT.

INCORPORATION OF SUPERHYDROPHOBIC MONOMERS IN WATERBORNE COATINGS"
F. Boscán, M. Meeuwisse, D. Mestach, M. J. Barandiaran, M. Paulis, S.J. Bohorquez
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RENEWABLE TERPENE DERIVATIVE AS A BIOSOURCED ELASTOMERIC BUILDING BLOCK IN THE DESIGN OF FUNCTIONAL ACRYLIC COPOLYMERS
S. Noppalit, A. Simula, N. Ballard, X. Callies, J.M. Asua, L. Billon.
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Submitted

IN-SITU PHOSPHATIZATION AND ENHANCED CORROSION PROPERTIES OF FILMS MADE OF PHOSPHATE FUNCTIONALIZED NANOPARTICLES" *Stefano Chimenti, Jesús Manuel Vega, Eva García-Lecina, Hans-Jürgen Grande, M. Paulis, J.R. Leiza*
REACT. FUNCT. POLYM.

SYNERGIC EFFECT OF SEMICRYSTALLINE NANODOMAINS AND IN-SITU PHOSPHATIZATION ON THE ANTICORROSION PROPERTIES OF WATERBORNE LATEXES"
S. Chimenti, J.M. Vega, E. García-Lecina, M. Paulis, J.R. Leiza
IND. ENG. CHEM. RES.

CRITICAL FILM FORMATION AND EVALUATION OF FLUORINATED-PHOSPHATE BASED WATERBORNE BINDER BY EIS AND SKP
S. Chimenti, J.M. Vega, E. García-Lecina, H.J. Grande, M. Paulis, J.R. Leiza
PROG. ORG. COAT.

OSTWALD RIPENING IN NANO/MINIEMULSIONS IN THE PRESENCE OF TWO COSTABILIZERS AS REVELED BY BROWNIAN DYNAMICS SIMULATIONS
Y. Reyes, S. Hamzehlou, J.R. Leiza
LANGMUIR

COUPLING HAADF-STEM TOMOGRAPHY AND IMAGE RECONSTRUCTION FOR THE PRECISE CHARACTERIZATION OF PARTICLE MORPHOLOGY OF COMPOSITE POLYMER LATEXES
N. Rajabalinia, S. Hamzehlou, E. Modin, A. Chuvilin, J.R. leiza, J.M. Asua
MACROMOLECULES

POLYURETHANE(PU)/ACRYLIC HYBRID WATERBORNE DISPERSIONS: SYNTHESIS, PROPERTIES AND APPLICATIONS
S. Mehravar, N. Ballard, R. Tomovska, J.M. Asua
IND. & ENG. CHEM. RES.

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The Hawkett group predominantly works with industry and presently has projects in areas as diverse as mining explosives, munitions, nanocomposites for paint, nanoparticles for biomedical applications, ionic liquid ferrofluids for space propulsion and agrochemical delivery systems. For fun: emulsion polymerisation kinetics and mechanisms.

Recently published papers

1. Nguyen Duc; Huynh Vien; Pham Nguyen; Pham Binh; Hawkett Brian; Serelis Algirdas; Davey Tim; Such Chris. SPION-Decorated Nanofibers by RAFT-Mediated Free Radical Emulsion Polymerization-Induced Self-Assembly. Macromolecular rapid Communications Volume: 40 Issue: 2 Special Issue: SI Article Number: 1800402 Published: JAN 2019.

   RAFT-mediated free-radical emulsion polymerization is successfully used to synthesize polystyrene nanofibers using triblock amphiphilic macro-RAFT copolymers as stabilizers. The polymerization is under RAFT control, producing various morphologies from spherical particles, nanofibers, nanoplatelets, and polymer vesicles. Optimum conditions are established for the synthesis of predominantly negatively charged polymer nanofibers. Superparamagnetic iron oxide nanoparticles (SPION)-decorated nanofibers are formed by simple mixing of the SPIONs with the fibers at an appropriate pH. The composite material has been found to be superparamagnetic and could be aligned under a magnetic field.

2. Pham, Binh T. T; Nguyen, Duc; Huynh, Vien T.; Pan, Eh Hau; Shirodkar-Robinson, Bhavna; Carey, Michelle; Serelis, Algirdas K.; Warr Gregory G.; Davey, Tim; Such, Christopher H.; Hawkett, Brian S. Aqueous Polymeric Hollow Particles as an Opacifier by Emulsion Polymerization Using Macro-RAFT Amphiphiles. Langmuir **2018**, 34, 14, 4255-4263.

   A robust polymerization technique that enables the surfactant-free aqueous synthesis of a high solid content latex containing polymeric hollow particles is presented. Uniquely designed amphiphilic macro-reversible addition fragmentation chain transfer

(RAFT) copolymers were used as sole stabilizers for monomer emulsification as well as for free-radical emulsion polymerization. The polymerization was found to be under RAFT control, generating various morphologies from spherical particles, wormlike structures to polymer vesicles. The final particles were dominantly polymeric vesicles which had a substantially uniform and continuous polymer layer around a single aqueous filled void. They produced hollow particles once dried and were successfully used as opacifiers to impart opacity into polymer paint films. This method is simple, can be performed in a controllable and reproducible manner, and may be performed using diverse procedures.

3. Priyananda, Pramith; Sabouri, Hadi; Jain, Nirmesh; Hawkett, Brian S. Steric Stabilization of gamma-Fe_2O_3 Superparamagnetic Nanoparticles in a Hydrophobic Ionic Liquid and the Magnetorheological Behaviour of the Ferrofluid. Langmuir, **2018**, 34, 9, 3068-3075.

   Hydrophobic ionic liquid ferrofluids (ILFFs) are studied for use in electrospray thrusters for microsatellite propulsion under nonatmospheric and in high-temperature environments. We synthesized a hydrophobic ILFF by dispersing sterically stabilized gamma-Fe2O3 nanoparticles (NPs) in the ionic liquid 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide. A diblock copolymer, C4-RAFT-AA(10)-DEAm60, was synthesized to facilitate multipoint bidentate anchoring to the NP through the acrylic acid block. The DEAm60 layer was incorporated to generate steric repulsion between particles to protect against the aggregation of magnetized particles arising from dipole-dipole attraction. The effect of shearing and variation in the magnetic field strength on the steric repulsion was examined using the DLVO theory. The effect of varying the magnetic field strength and particle concentration on the viscoelastic properties of the ferrofluid was evaluated using rheometry. The viscosity of the ferrofluid increased with the magnetic field strength, indicating that the magnetized particles assembled into a structure. The level of straining required to break down the structure formed by the magnetized particles increased with the magnetic field strength and particle concentration. The absence of particle interlocking during shearing was indicated by the smooth viscosity versus shear rate traces. The DLVO analysis showed that increasing the magnetic attraction between the particles causes the DEAm60 brush layers on the particles to overlap more, resulting in an increase in the steric repulsion. As overlapping increases, osmotic repulsion is caused before progressing to a strong elastic repulsion. The effect of the polymer solubility and particle interaction due to hydrodynamic forces on the steric repulsion was also analysed.

4. Alex M. Djerdjev, Pramith Priyananda, Jeff Gore, James K. Beattie, Chiara Neto and Brian S. Hawkett. The mechanism of the spontaneous detonation of ammonium nitrate in reactive grounds. Journal of Environmental Chemical Engineering. 6, 1, **2018**, Pages 281-288

   The mechanism of the decomposition of ammonium nitrate fuel oil (ANFO) and of ammonium nitrate (AN) emulsions has been investigated. The formation of NO gas bubbles at the end of an induction period was observed, which led to the evolution of brown NO2 gas on contact with air. Inhibition of the decomposition reaction could be achieved by reducing the NO concentration in the gas phase, with inhibitors not in physical contact with the reaction mixture. NO adsorbing clay minerals (hydrotalcite) were effective inhibitors, indicating multiple mechanisms of inhibition. A central role is assigned to nitrous acid (HNO2): sequestering NO prevents its formation, base inhibitors keep it in the non-reactive form of the nitrite ion (pKa of HNO2 similar to 3), and urea in acidic conditions decomposes it to harmless N-2. Our results have implications in industries where NOx emissions can cause significant environmental problems for both aquatic and marine life as well as for human health.

5. Binh T. T. Pham, Emily K. Colvin, Nguyen T. H. Pham, Byung J. Kim, Emily S. Fuller, Elizabeth A. Moon, Raphael Barbey, Samuel Yuen, Barry H. Rickman, Nicole S. Bryce, Stephanie Bickley, Marcel Tanudji, Stephen K. Jones, Viive M. Howell, and Brian S. Hawkett. Biodistribution and Clearance of Stable Superparamagnetic Maghemite Iron Oxide Nanoparticles in Mice Following Intraperitoneal Administration. Int. J. Mol. Sci. **2018**, 19,

   Nanomedicine is an emerging field with great potential in disease theranostics. We generated sterically stabilized superparamagnetic iron oxide nanoparticles (s-SPIONs) with average core diameters of 10 and 25 nm and determined the in vivo biodistribution and clearance profiles. Healthy nude mice underwent an intraperitoneal injection of these s-SPIONs at a dose of 90 mg Fe/kg body weight. Tissue iron biodistribution was monitored by atomic absorption spectroscopy and Prussian blue staining. Histopathological examination was performed to assess tissue toxicity. The 10 nm s-SPIONs resulted in higher tissue-iron levels, whereas the 25 nm s-SPIONs peaked earlier and cleared faster. Increased iron levels were detected in all organs and body fluids tested except for the brain, with notable increases in the liver, spleen, and the omentum. The tissue-iron returned to control or near control levels within 7 days post-injection, except in the omentum, which had the largest and most variable accumulation of s-SPIONs. No obvious tissue changes were noted although an influx of macrophages was observed in several tissues suggesting their involvement in s-SPION sequestration and clearance. These results demonstrate that the s-SPIONs do not degrade or aggregate in vivo and intraperitoneal administration is well tolerated, with a broad and transient biodistribution. In an ovarian tumour model, s-SPIONs were shown to accumulate in the tumours, highlighting their potential use as a chemotherapy delivery agent.

6. Aaron Madden, Juan Fernandez de la Mora, Nirmesh Jain, Hadi Sabouri and Brian Hawkett. Effect of a homogeneous magnetic field on the electrospraying characteristics of sulfolane ferrofluids. Journal of Fluid Mechanics, **2017**, 833, 430-444.

   We explore the effect of an applied homogeneous magnetic field on the electrospraying characteristics of a ferrofluid in the cone-jet mode. A sulfolane-based ferrofluid mixed with the ionic liquid ethyl ammonium nitrate has been synthesized. These mixtures have negligible volatility under ambient conditions and remain stable under a very wide range of electrical conductivities K. Magnetized Taylor cones spray with the same current emission characteristics as their non-magnetized counterparts in the shared voltage and flow rate parameter space. However, the magnetized Taylor cones studied remained stable at voltages 23% lower than the non-magnetized spray; they also access flow rates 30% and 40% lower in ferrofluids with K = 0.3 and 0.01 S.m(-1). In the lower voltage ranges available only to magnetized tips, unusually long stable cones are observed. The magnetic stabilization mechanism responsible for these two effects remains unclear. It is noteworthy that these strong effects arise even when the tip curvature of the strictly magnetized liquid is orders of magnitude smaller than that for the strictly electrified liquid.

7. Andre L Samson, Imala Alwis, Jessica A. A. Maclean, Pramith Priyananda, Brian Hawkett, Simone M Schoenwaelder and Shaun P Jackson. Endogenous fibrinolysis facilitates clot retraction in vivo. BLOOD **2017** 130, 23, 2453-2462.

   Clot retraction refers to the process whereby activated platelets transduce contractile forces onto the fibrin network of a thrombus, which over time increases clot density and decreases clot size. This process is considered important for promoting clot stability and maintaining blood vessel patency. Insights into the mechanisms regulating clot retraction at sites of vascular injury have been hampered by a paucity of in vivo experimental models. By pairing localized vascular injury with thrombin microinjection in the mesenteric circulation of mice, we have demonstrated that the fibrin network of thrombi progressively compacts over a 2-hour period. This was a genuine retraction process, as treating thrombi with blebbistatin to inhibit myosin IIa-mediated platelet contractility prevented shrinkage of the fibrin network. Real-time confocal analysis of fibrinolysis after recombinant tissue-type plasminogen activator (tPA) administration revealed that incomplete proteolysis of fibrin polymers markedly facilitated clot retraction. Similarly, inhibiting endogenous fibrinolysis with tranexamic acid reduced retraction of fibrin polymers in vivo. In vitro clot retraction experiments indicated that subthreshold doses of tPA facilitated clot retraction through a plasmin-dependent mechanism. These effects correlated with changes in the elastic modulus of fibrin clots. These findings define the endogenous fibrinolytic system as an important regulator of clot retraction, and show that promoting clot retraction is a novel and complementary means by which fibrinolytic enzymes can reduce thrombus size.

Contribution: Dr. Stuart Thickett

Contribution to IPCG Newsletter – Spring 2019

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Research Focus

Our research group focuses on the physical chemistry of soft matter, specifically polymers, colloids, nanoparticles and thin films. We are interested using fundamental kinetic and mechanistic knowledge to create new materials with specific properties and attributes. We utilize advanced polymer synthesis, surface and interfacial phenomena, as well as colloidal and particle interactions in a variety of applications.

Research Themes:

- Polymer and Colloid Engineering for Preparing Colloidal Nanocomposites
- Functional Surface Coatings Using Thin Film Dewetting
- Nanomaterials and Functional Polymer Monoliths

Recent Graduates

Dr Guo Hui (Chris) Teo, Doctor of Philosophy 2018, University of Tasmania
Thesis topic: Polymer-Inorganic Hybrid Nanoparticles via Polymerization-Induced Self-Assembly

Recently Published Papers (2018-onwards)

- **Thickett, S.C.* and Teo, G.H.** *Recent Advances in Colloidal Nanocomposite Design via Heterogeneous Polymerization Techniques,* Polymer Chemistry (Pioneering Investigators Special Issue), *in press* (DOI: 10.1039/C9PY00097F).
- Teo, G.H., Zetterlund, P.B. and **Thickett, S.C.*** *Interfacial Cross-Linking of Self-Assembled Triblock Copolymer Nanoparticles via Alkoxysilane Hydrolysis and Condensation,* Journal of Polymer Science Part A: Polymer Chemistry, *in press* (DOI: 10.1002/pola.29313).
- Sutton, A.T., Arrua, R.D., **Thickett, S.C.,** Lombi, E. and Hilder, E.F. *Understanding the Interaction of Gold and Silver Nanoparticles with Natural Organic Matter Using Affinity Capillary Electrophoresis,* Environmental Science: Nano, **2019,** 6, 1351-1362 (DOI: 10.1039/C9EN00014C).

- Cai, Y., Fadil, Y., Jasinski, F., Agarawl, V., **Thickett, S.C.** and Zetterlund, P.B. *Miniemulsion Polymerization Using Graphene Oxide as Surfactant: In Situ Grafting of Polymer,* Carbon, **2019,** 149, 445-451 (DOI: 10.1016/j.carbon.2019.04.063)
- Fadil, Y., Minami, H., Agarwal, V., Jasinski, F., **Thickett, S.C.** and Zetterlund, P.B. *Electrically Conductive Polymer/rGO Nanocomposite Films and Ambient Temperature via Miniemulsion Polymerization Using GO as Surfactant,* Nanoscale, **2019,** 11, 6566-6570 (DOI: 10.1039/C9NR00816K).
- Fadil, Y., Jasinski, F., Guok, T.L., **Thickett, S.C.**, Minami, H. and Zetterlund, P.B. *Pickering Miniemulsion Polymerization Using Graphene Oxide: Effect of Addition of Conventional Surfactant,* Polymer Chemistry, **2018,** 9, 3368-3378 (DOI: 10.1039/C8PY0067A).
- Jasinski, F., Alkhater, A., **Thickett, S.C.,** Brinkhuis, R. and Zetterlund, P.B. *Estimation of Copolymer/Water Interfacial Tensions Using Pendant Drop Tensiometry,* Langmuir, **2018,** 34, 6835-6843 (DOI: 10.1021/acs.langmuir.8b00554).
- Pullen, R.,* **Thickett, S.C.*** and Bissember, A.C.* Investigating the Viability of a Competency-Based, Qualitative Laborartory Assesment Model in First Year Undergraduate Chemistry, Chemistry Education Research and Practice, **2018,** 19, 629-637 (DOI: 10.1039/C7RP00249A).
- Teo, G.H., Kuchel, R.P., Zetterlund, P.B. and **Thickett, S.C.*** Self-Assembly of Block Copolymers With an Alkoxysilane-Functional Core-Forming Block: A Comparison of Synthetic Approaches, Journal of Polymer Science Part A: Polymer Chemistry, **2018,** 56, 420-429 (DOI: 10.1002/pola.28911).
- Khodabandeh, A., Arrua, R.D., Coad, B.R., Rodemann, T., Ohigashi, T., Kosugi, N., **Thickett, S.C.** and Hider, E.F. Morphology Control in Polymerized High Internal Phase Emulsion Templated via macro-RAFT Agent Composition: Visualizing Surface Chemistry, Polymer Chemistry, **2018**, 9, 213 (DOI: 10.1039/C7PY01770G).

Full Publication List

https://scholar.google.com.au/citations?user=QstVw50AAAAJ&hl=en

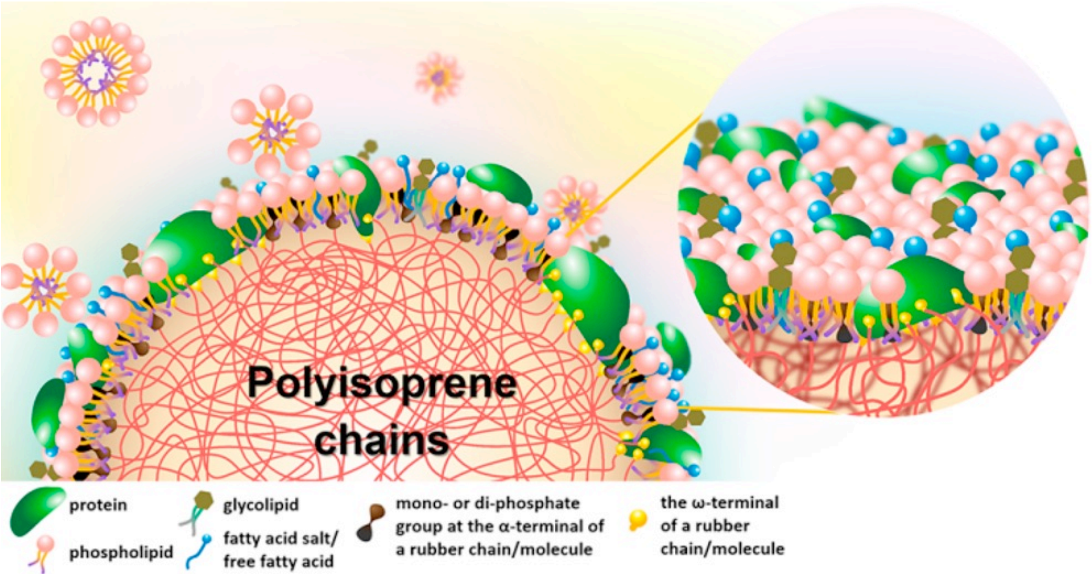
Contribution: Dr. C. C. Ho

Investigating the Mechanistic and Structural Role of Lipid Hydrolysis in the Stabilization of Ammonia-Preserved *Hevea* Rubber Latex

Sirirat Kumarn, Nut Churinthorn, Adun Nimpaiboon, Manus Sriring, Chee-Cheong Ho,
Atsushi Takahara, and Jitladda Sakdapipanich

Langmuir 2018, 34, 12730−12738

ABSTRACT: The stabilization mechanism of natural rubber (NR) latex from *Hevea brasiliensis* was studied to investigate the components involved in base-catalyzed ester hydrolysis, namely, hydrolyzable lipids, ammonia, and the products responsible for the desired phenomenon observed in ammonia-preserved NR latex. Latex stability is generally thought to come from a rubber particle (RP) dispersion in the serum, which is encouraged by negatively charged species distributed on the RP surface. The mechanical stability time (MST) and zeta potential were measured to monitor field latices preserved in high (FNR-HA) and low ammonia (FNRLA) contents as well as that with the ester-containing components removed (saponified NR) at different storage times. Amounts of carboxylates of free fatty acids (FFAs), which were released by the transformation and also hypothesized to be responsible for the like-charge repulsion of RPs, were measured as the higher fatty acid (HFA) number and corroborated by confocal laser scanning microscopy (CLSM) both qualitatively and quantitatively. The lipids and their FFA products interact differently with Nile red, which is a lipid-selective and polarity-sensitive fluorophore, and consequently re-emit characteristically. The results were confirmed by conventional ester content determination utilizing different solvent extraction systems to reveal that the lipids hydrolyzed to provide negatively charged fatty acid species were mainly the polar lipids (glycolipids and phospholipids) at the RP membrane but not those directly linked to the rubber molecule and, to a certain extent, those suspended in the serum. From new findings disclosed herein together with those already reported, a new model for the *Hevea* rubber particle in the latex form is proposed.



Contribution: Dr. Maud Save

Contribution to the Fall 2018 IPCG Newsletter

Dr. Maud Save
IPREM, CNRS, University of Pau & Pays Adour, UMR 5254, ,2 avenue du Président Angot, Pau, F-64053, France
https://iprem.univ-pau.fr/en/_plugins/mypage/mypage/content/msave.html

List of recently published articles

“Tuning photosensitized singlet oxygen production from microgels synthesized by polymerization in aqueous dispersed media”
Luca Petrizza, Mickael Le Bechec, Emile Decompte, Hind El Hadri, Sylvie Lacombe*, Maud Save* *Polymer Chemistry* **2019**, *10*, DOI: 10.1039/C9PY00157C (2019 Polymer Chemistry Pioneering Investigators Issue)

Abstract

Novel sub-micronic photoactive polymer colloids grafted with Rose Bengal (RB) photosensitizer were designed to promote singlet oxygen production from a supported organic photosensitizer. Photooxygenation of fine chemicals under visible light irradiation is considered as a green process. To enhance the overall process sustainability, stable colloidal particles were synthesized by polymerization in aqueous dispersed media with the ability to be transferred into ethanol, recycled by a centrifugation step and reused with no significant decrease of the quantum yield of singlet oxygen production. The microgels were synthesized for the first time by miniemulsion copolymerization of vinyl acetate (VAc), N-vinyl caprolactam (VCL), polymerizable vinyl benzyl Rose Bengal (VBRB) monomers and divinyl adipate (DVA) crosslinker. The microgels were characterized by UV-visible spectroscopy and compared with the homologue non-crosslinked polymer in order to discriminate the effect of RB grafted onto the linear polymer from its grafting inside crosslinked microgels. The quantum yields of singlet oxygen production were almost null in water but interestingly in the range of 0.27-0.47 in ethanol. The singlet oxygen quantum yield of these polymer materials is tuned by the aggregation state of VBRB units, hence producing an ON/OFF photosensitizing colloidal system. The absorption and emission spectra of the VBRB containing microgels in water were characteristic of strongly aggregated VBRB, while no evidence of aggregation was observed from the spectra in ethanol. The highest singlet oxygen quantum yield of the linear polymer was correlated with a less aggregated state of RB units compared with the crosslinked microgels. The present RB-based microgels were 20 % more resistant to photobleaching than free RB.

“Latex Stabilized by Unmodified Cellulose Nanocrystals: Role of Monomers on Particle Size”
Clara Jiménez-Saelices, Maud Save, Isabelle Capron* *Polymer Chemistry* **2019**, *10*, 727 - 737

Abstract

Cellulose nanocrystals (CNCs) are sustainable rod-shaped nanoparticles able to adsorb at oil-water interfaces to produce highly stable Pickering emulsions with enhanced mechanical properties. Polymerization of the CNC-stabilized monomer droplets is investigated in details to elucidate the synthesis mechanism of both micro- and nanoparticles of latex in relationship with the initial sizes of the droplets. It is shown in this study that unmodified CNCs, used as sole stabilizer, are efficient to produce both monomer-in-water Pickering emulsion and nanocomposite latex particles with controlled dimensions. For the initial liquid emulsion of styrene, two populations of droplets were observed: micrometric droplets with diameters that decrease down to 5 µm with increasing CNC concentrations, and nanometric droplets with a diameter distribution ranging from 500 nm to 2 µm for all CNC concentrations. It leads to two distinct populations of polystyrene latex particles by polymerization in aqueous dispersed media, i.e. microparticles of 5-18 µm and nanoparticles with an average diameter below 1 µm. The polymerization of various monomers, i.e. styrene, lauryl methacrylate, isobornyl Acrylate, butyl methacrylate, methyl methacrylate, in the presence of different initiators highlighted that the solubility of the monomer in the aqueous continuous phase is the key parameter to tune the size distribution of the latex particles. Nanocomposite CNC-stabilized waterborne latexes were prepared from polymer with different glass transition temperatures.

"Transparent polymer nanocomposites: an overview on their synthesis and advanced properties"
Julien Loste, José Lopez-Cuesta, Laurent Billon, Hélène Garay,* Maud Save* *Progress in Polymer Sciences.* **2019**, *89*, 133-158.

Abstract

Since the last decade, there has been an increasing demand for the design of more advanced functional materials. The integration of inorganic nanoparticles to polymer matrices is a powerful tool to confer their fascinating and complementary properties to the polymer materials. Among the different polymer nanocomposites, transparent nanocomposites have gained a growing interest as a result of their significant importance for a wide range of applications. In order to achieve the high level of transparency, it is of paramount importance to minimize the aggregation of the nanoparticles inducing significant light scattering hampering the application for transparent materials. The basic concepts of light scattering, the refractive index modulation and the methods to characterize the transparency of nanocomposites are provided to introduce this review. The elaboration of the transparent nanocomposites has been the subject of many efforts to develop methods to limit aggregation. To address this challenge, several methods have been implemented to control the polymerization process, the nanoparticle synthesis, the polymer-nanoparticle interface together with the polymer casting or processing. The main methodologies developed to elaborate transparent nanocomposites are discussed according to four main categories: the blending of nanoparticles and polymer, the in-situ polymerization in the presence of pre-formed nanoparticles, the in-situ nanoparticle synthesis in a pre-formed polymer matrix and finally the simultaneous polymerization and in-situ nanoparticle synthesis. The more scarce studies dealing with casting of polymer solution loaded with core-shell nanoparticles are also discussed. In light of the literature on polymer nanocomposites, this review focuses mainly on transparent nanocomposites with a special attention given to the level of transparency and how this transparency is assessed for each study claiming transparency of the nanocomposite. For each class of nanocomposites, it is of great importance to provide an overview of the different level of transparency according to the thickness of the polymer material. The second part of the review provides a thorough overview of the properties investigated in transparent nanocomposites with attention paid to the characterization of transparency. The transparent nanocomposites were

described according to the targeted properties which are primarily the improvement of mechanical properties, thermal stability, barrier properties, magnetic properties and the optical properties. The optical properties have been the most thoroughly investigated thanks to the myriad of inorganic nanoparticles exhibiting excellent wide range of optical properties. Thus, the present review also describes the polymer/nanoparticle systems designed for the elaboration of transparent polymer nanocomposites with advanced optical properties: UV or IR-filtering properties, photoluminescence, ability to produce extreme refractive index, dichroism or non-linear optical properties.

PhD Theses in progress

Charlène Boussiron, Oct 2016 – Sept 2019
"Design of photo-active polymer nanoparticles by polymerization in aqueous dispersed media"
Supervisors: Dr. Maud Save and Dr. Sylvie Lacombe.
IPREM (CNRS, University of Pau, France)

Emile Decompte, Oct 2016 – Sept 2019
"Controlled synthesis of polymer colloids by miniemulsion polymerization for selective recognition of organic contaminants"
Supervisors: Dr. Maud Save and Dr. Elise Deniau
IPREM (CNRS, University of Pau, France). Collaboration with team of analytical chemistry of IPREM.

Ismail Adoumaz, Jan 2017 – Jan 2020
"Synthesis of polylactide-based copolymers by bulk and miniemulsion polymerization"
Joint Doctorate Program, University of Pau, France and University of Cadii Ayad, Marrakech

Valentine Devilledon, Oct 2018 – Sept 2021
"Biobased waterborne latex for Pickering emulsions"
IPREM (CNRS, University of Pau, France), CRPP (CNRS, University of Bordeaux)

Contribution: Dr. François Ganachaud

DR. F. Ganachaud

I am currently on Sabbatical Leave in the USA, in a joint lab CNRS/UPenn/Solvay, in Bristol (Pennsylvania) until December 2019. My theme of research here concerns the encapsulation of hydrophilic actives.

Articles in preparation

GlycoNanoCapsules: Synthesis and Applications

Xibo Yan, Luxiao Chai, Etienne Fleury, François Ganachaud and Julien Bernard

Chem. Rev., to be submitted (2019)

Abstract: In this article, we report on the recent achievements on glyconanocapsules design and their use in biomedical applications. The present manuscript covers all the important strategies for constructing core/shell structured carbohydrate-based nano-objects, from naturally-occurring polysaccharides to synthetic glycopolymers. We first start by exhaustively reviewing all reported chemical or/and physical approaches to glyconanocapsules as well as glyco-polymersomes, including popular methods such as i) self-assembly of amphiphilic copolymers into polymersomes or micelles (then followed by a selective removal of the core); ii) layer-by-layer deposition of polymers on sacrificial template particles; iii) interfacial polymerization under miniemulsion conditions, and iv) other (new coming) technologies. According to the techniques of preparation, the reservoir of capsules can be filled either with water (chapter 2) or oil (chapter 3). The final part addresses the biomedical applications of these glyconanocapsules (chapter 4), including i) specific recognition or interaction with proteins for targeting delivery; ii) shielding of the nanocarriers from general proteins absorption to increase the circulation time; iii) practical bio-imaging tools for visualizing physiological reactions; and iv) potent nanocarriers for drug and gene delivery.

Nanocapsules with Mixed-/Multilayered-Polysaccharide Shells through Simultaneous/ Sequential Nanoprecipitation Steps

Xibo Yan, Pierre Alcouffe, Luis Munoz, Rostyslav Bilyy, Ricardo Ramos, François Ganachaud and Julien Bernard

Submitted (June 2019)

Abstract: Oil-filled polymer nanocapsules made of conventional, neutral polysaccharides are not available nowadays. We present here a universal way of precipitating and crosslinking any type of commercial polysaccharides onto oil droplets by the so-called solvent shifting process. Thanks to thoroughly derived phase diagrams, monocomponent or multicomponent shells of mixed or sequentially coated polymers are produced in one-pot, without the need for extensive purification and/or concentration. The capsules are non-toxic, can be readily functionalized inside and outside of the shell to anticipate further bio-applications.

Recently published articles and patent

AQUEOUS CATIONIC HOMO- AND CO-POLYMERIZATIONS OF B-MYRCENE AND STYRENE: A GREEN ROUTE TOWARD TERPENE-BASED RUBBERY POLYMERS

Maksim I Hulnik, Irina V Vasilenko, Alexei V Radchenko, Frederic Peruch, Francois Ganachaud, Sergei V Kostjuk,.

Polymer Chemistry **2018***, 9*, 5690-5700.

Abstract*:* Aqueous cationic polymerization of β-myrcene, a naturally occurring monomer, was performed for the first time using a water-dispersible Lewis acid surfactant combined catalyst (LASC) prepared from ytterbium chloride and a branched sodium dodecylbenzenesulfonate surfactant. At 40 °C, poly(β-myrcene)s of high molecular weight (M_n up to 150 kg mol^{-1}) and low glass transition temperature ($T_g < -63$ °C) were obtained. They possess predominantly 1,4-units (~43% *cis* and ~50% *trans*) and few 3,4-units (~7%) together with both regular head-to-tail (62–72%) and inverse (5–10% head-to-head and 23–28% tail-to-tail) sequences. The LASC showed also high efficiency in catalyzing the emulsion cationic copolymerization of β-myrcene and styrene, affording the synthesis of random copolymers with high molecular weights (M_n from 60 to 120 kg mol^{-1}) and single glass transition temperatures (T_g's from −43 to 15 °C). Finally, a simple procedure was developed to recover the catalyst from the reaction mixture, which showed high activity in the β-myrcene emulsion cationic polymerization even after five successive cycles of extraction.

Work in progress (in emulsion)

Ricardo RAMOS (Ph. D., 3rd year): *Synthesis of Injectable Nanocapsules Loaded with Drugs*

Sergei KOSTJUK (Invited Professor, industrial project): *Cationic Polymerization in Emulsion of a Specific Halogenated Monomers*

Lerys GRANADO (1 year Post-Doc, academic project): *Water-in-water nanocapsules*

Contribution: Prof. Michael Cunningham

Spring 2019

Reported by:
Michael F. Cunningham
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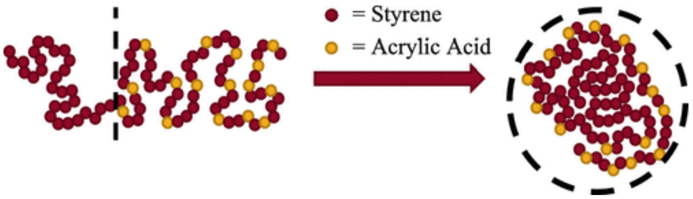
In Press

2. Sanders, Connor A.; George, Sean R.; Deeter, Gary A.; Campbell, J. D.; Reck, Bernd; Cunningham, Michael F. Amphiphilic Block-Random Copolymers: Self-Folding Behavior and Stabilizer in Emulsion Polymerization, Macromolecules, in press

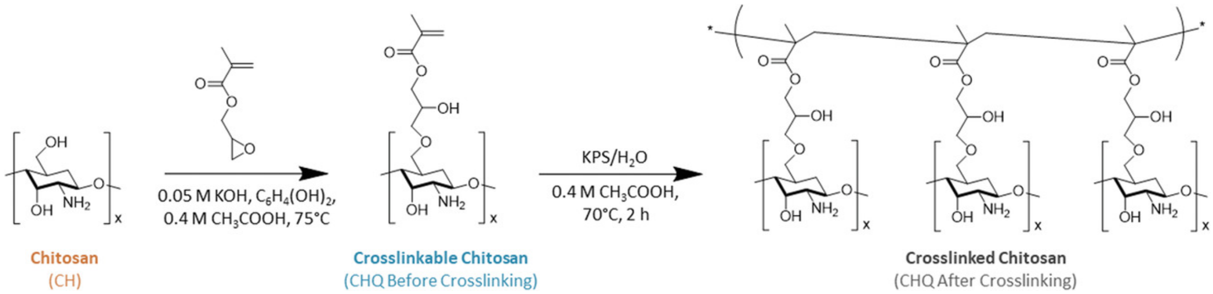
Abstract: Polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers have been synthesized at various molecular weights (7000–23 200 g/mol) and with compositions between 6 and 39 mol % acrylic acid by nitroxide-mediated polymerization. Emulsion polymerizations of styrene stabilized by block-random copolymers yielded stable latexes at stabilizer concentrations ≥3 wt % based on monomer. A series of emulsion polymerizations with varying stabilizer content suggests that a novel nucleation mechanism occurs in block-random copolymer-stabilized emulsion polymerizations, exhibiting distinctly different behaviors from block copolymers or conventional small-molecule surfactants. Moreover, alkaline aqueous dispersions of the block-random copolymers were prepared with ease up to concentrations of 300 g/L, whereas similar block copolymers are limited to ∼1 g/L. Analysis of the dispersions via dynamic light scattering and atomic force microscopy suggests that single-chain nanoparticles form via a self-folding process with hydrodynamic diameters between 2.4 and 5 nm. The novel stabilizer structures may be tuned for rapid dispersion through their anchoring block [polystyrene] and high stabilization efficiency through the stabilizing block [polystyrene-r-poly(acrylic acid)].



1. Lazar, Simone; Garcia-Valdez, Omar; Kennedy, Emily; Champagne, Pascale; Cunningham, Michael F.; Grunlan, Jaime C.. Crosslinkable Chitosan Enabled

Moisture-Resistant Multilayer Gas Barrier Thin Film, Macromolecular Rapid Communications, in press

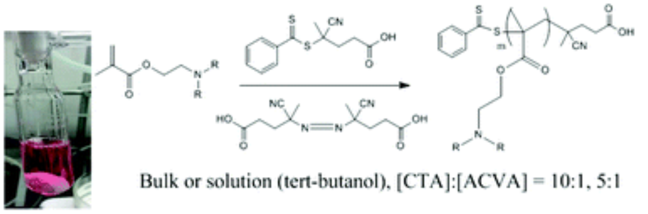
Abstract: Chitosan-based films exhibit good oxygen barrier that degrades when exposed to high humidity. In an effort to overcome this drawback, a multilayer nanocoating consisting of crosslinkable chitosan (CHQ) and poly(acrylic acid) [PAA] is deposited on polyethylene terephthalate (PET) using layer-by-layer assembly. Chitosan is functionalized with glycidyl methacrylate to introduce acrylic functionalities within the film. The deposited films are crosslinked using a free radical initiator and this crosslinking is confirmed by FTIR and reduced film thickness. A 10-bilayer (BL) crosslinked CHQ/PAA film, which is only 165 nm thick, results in a 36× reduction of the oxygen transmission rate of PET at 90% relative humidity. To achieve these same results without crosslinking, a 15-BL unmodified chitosan (CH)/PAA film, which is almost 5× thicker, must be deposited on PET. This environmentally friendly, transparent nanocoating is promising for food packaging or protection of flexible electronics, especially in high-humidity environments.



Recent Publications

Arredondo, Jaquin; Champagne, Pascale; Cunningham, Michael F.. RAFT-mediated polymerisation of dialkylaminoethyl methacrylates in tert-butanol, Polymer Chemistry (2019), 10, 1938-1946.

Abstract: Polymerisation of dialkylaminoethyl methacrylates by reversible deactivation radical polymerisation (RDRP) provides a route for the synthesis of block polymers or macro-initiators/macro-chain transfer agents for subsequent grafting onto various substrates. While ATRP and NMP can be used to polymerise these monomers, limitations have been reported. With ATRP, the monomers have a strong affinity for the copper-based catalysts, compromising the livingness of the polymerisation. Additionally, polar solvents often cannot be employed due to solubility limitations or side reactions. In the case of NMP, a comonomer (usually styrene) is necessary to achieve good control for the polymerisation of methacrylates. RAFT-mediated polymerisation offers advantages for amino-containing monomers, yielding pure homopolymers in well controlled polymerisations. In this work, we report for the first time on the polymerisation of dialkylaminotethyl methacrylates in *tert*-butanol, where good control and livingness were confirmed by GPC-UV-RI analysis and chain extension experiments.


Bulk or solution (tert-butanol), [CTA]:[ACVA] = 10:1, 5:1

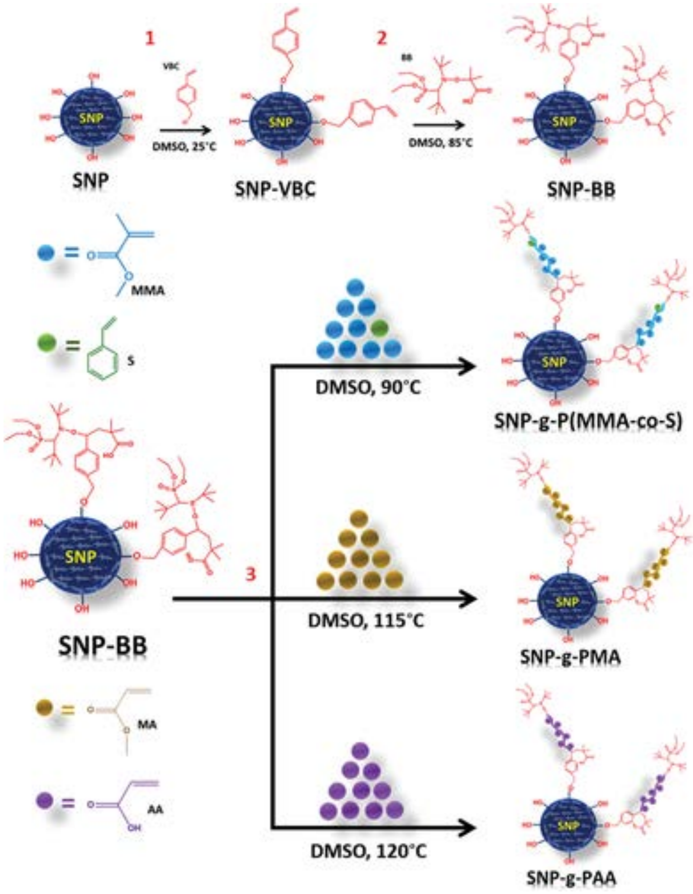
Giudici, Reinaldo; Espinola, Magda; Cunningham, Michael. Preparation of thermochromic films from latexes made by miniemulsion polymerization, Macromolecular Reaction Engineering (2019), 13, 1900009, DOI: 10.1002/mren.201900009.

Abstract: Thermosensitive-thermochromic pigments are classified as smart materials capable of detecting and/or responding to environmental stimuli, and specifically in this study, changes in temperature that induce a change in the color of the material. This study aims to obtain nanoparticles of poly(styrene-co-butyl acrylate) and poly(styrene-co-methyl methacrylate), containing thermosensitive-thermochromic pigments that are incorporated into the monomer droplets in miniemulsion polymerization. Miniemulsion polymerization has the advantage that the pigment particles can be dispersed directly in the monomer droplets and are encapsulated when the miniemulsion droplets are polymerized. Using controlled/living radical polymerization (or Reversible Deactivation Radical Polymerization), it is possible to produce polymers with better control of microstructure and narrower molecular weight distributions. Nitroxide-mediated polymerization (NMP) is conducted using the BlocBuilder initiator, as well as a conventional free radical polymerization (FRP) using potassium persulfate (KPS) and 2,2-azobis(2-methylpropionitrile) (AIBN). Stable latexes containing the thermosensitive-thermochromic pigments are obtained by both NMP and FRP. Films are made from the latexes and shown to exhibit thermochromic behavior.

Cazotti, Jaime C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dube, Marc A.; Cunningham, Michael F. Grafting from Starch Nanoparticles with Synthetic Polymers via Nitroxide-mediated Polymerization, Macromolecular Rapid Communications (2019), 10, 1800834. [Invited]

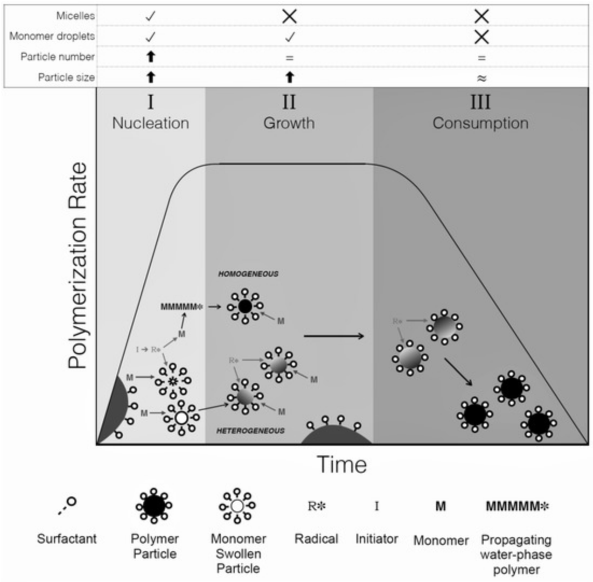
Abstract: Nitroxide-mediated polymerization (NMP) is employed to graft synthetic polymers from polysaccharides. This work demonstrates the first successful polymer grafting from starch nanoparticles (SNPs) via NMP. To graft synthetic polymers from the SNPs' surface, the SNPs are first functionalized with 4-vinylbenzyl chloride prior to reaction with BlocBuilder MA yielding a macroinitiator. Methyl methacrylate with styrene, acrylic acid, or methyl acrylate are then grafted from the SNPs. The polymerizations exhibited linear reaction kinetics, indicating that they are well controlled. Thermal gravimetric analysis and spectroscopic techniques confirmed the synthesis of the precursors materials and the success of the grafting from polymerizations. The

incorporation of hydrophobic synthetic polymers on hydrophilic SNPs yields new hybrid materials that could find use in several industrial applications including paper coatings, adhesives, and paints.



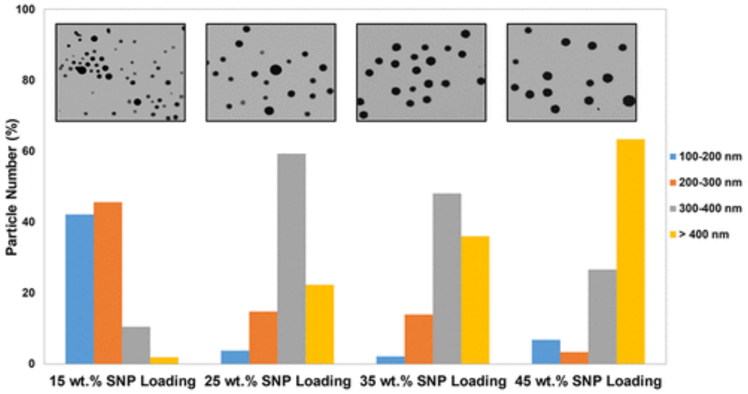
Cummings, Shidan; Zhang, Yujie; Smeets, Niels; Cunningham, Micheal; Dubé, Marc A.. On the Use of Starch in Emulsion Polymerizations, Processes (2019), 7, 140, DOI: 10.3390/pr7030140.

Abstract: The substitution of petroleum-based synthetic polymers in latex formulations with sustainable and/or bio-based sources has increasingly been a focus of both academic and industrial research. Emulsion polymerization already provides a more sustainable way to produce polymers for coatings and adhesives, because it is a water-based process. It can be made even more attractive as a green alternative with the addition of starch, a renewable material that has proven to be extremely useful as a filler, stabilizer, property modifier and macromer. This work provides a critical review of attempts to modify and incorporate various types of starch in emulsion polymerizations. This review focusses on the method of initiation, grafting mechanisms, starch feeding strategies and the characterization methods. It provides a needed guide for those looking to modify starch in an emulsion polymerization to achieve a target grafting performance or to incorporate starch in latex formulations for the replacement of synthetic polymers.



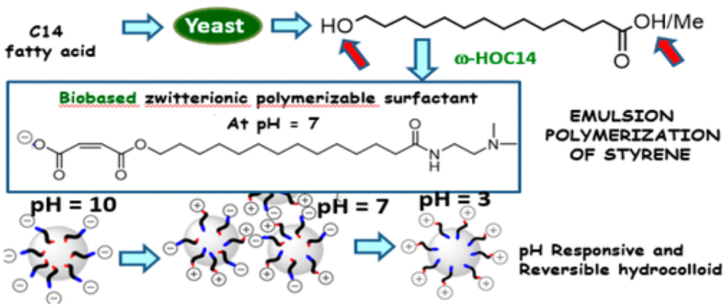
Zhang, Yujie; Cunningham, Michael F.; Smeets, Niels M.B.; Dubé, Marc A.. Increasing Starch Nanoparticle Content in Emulsion Polymer Latexes, Industrial & Engineering Chemistry Research (2019), DOI: 10.1021/acs.iecr.9b00332.

Abstract: Starch nanoparticles (SNPs) were used to partially replace petroleum-based polymers in a biobased latex adhesive application. Modification of SNPs (i.e., increasing cross-link density, functionalizing using a sugar-based monomer, and tuning SNP hydrophobicity) was performed prior to their incorporation in a semibatch emulsion polymerization to produce stable SNP-based latexes. SNP loadings and latex solids content were varied to study their effect on latex stability and properties (e.g., viscosity, particle size, adhesive properties, particle morphology). Stable and low viscosity latexes with up to 45 wt % SNP loadings and 55 wt % latex solids were achieved. STEM images confirmed the presence of the core–shell morphology, where SNPs were located in the particle cores and provided biocontent, while the acrylic polymers were present as the shell and governed the application properties. Pushing the limits of SNP loading and latex solids was shown to come at a cost to adhesive and other properties.



Hu, Jing; Sanders, Connor; Mekala, Shekar; Chen, Tzu-Yin; Cunningham, Michael F.; Gross, Richard A.. A Zwitterionic Polymerizable Surfactant from omega-Hydroxyltetradecanoic Acid Provides Stimuli Responsive Behavior, Macromolecules (2019), 52, 1517 – 1525.

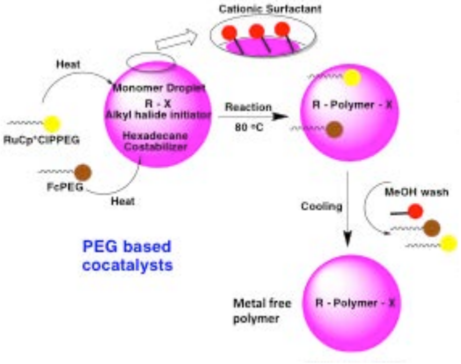
Abstract: ω-Hydroxytetradecanoic acid (ω-HOC14), prepared via an efficient yeast-catalyzed ω-hydroxylation of the corresponding fatty acid, was converted in two steps to the polymerizable zwitteronic surfactant ω-O-maleate-α-2-dimethylaminoethyl tetradecanamide (DMTA). Emulsion polymerizations of styrene with DMTA, bearing carboxylic and tertiary amine groups at the ω- and α-positions, were conducted in different pH environments. Emulsion polymerizations were most successful (particle diameters <80 nm, high styrene conversion) under basic conditions (pH 9.8 and 11.0), where latex samples have highly negative zeta potentials (−40.4 to −46.0 mV). Because of the zwitterionic nature of the surfactant, transparent or semitransparent latexes were obtained under either acidic (pH < 4) or basic (pH > 9) conditions. In the pH range of 4–9, aggregation occurred; however, by adjustment of the pH to either acidic or basic conditions, partial redispersion occurred highlighting DMTA's ability to provide stimuli-responsive colloidal behavior. Unexpectedly, upon drying the latex formed at pH = 3.1, a membrane with nanodimension pores was formed.



Elijah Bultz, Makoto Ouchi, Mitsuo Sawamoto and Michael F. Cunningham. Smart catalysis with thermoresponsive ruthenium catalysts for miniemulsion living radical polymerization cocatalyzed by smart iron cocatalysts, Journal of Polymer Science, Polymer Chemistry Edition (Part A) (2019) 57, 305-312. [Invited]

Abstract: This work reports the use of cocatalysts in addition to 'smart' ruthenium catalysts for Ru-mediated reversible deactivation radical polymerization (RDRP) in miniemulsion, allowing for the synthesis of final products with significantly reduced residual metal. Using amine cocatalysts in miniemulsion allows for high conversions (> 90%) in under 10 hours. Two forms of ferrocene cocatalysts are also used, including 'smart' thermoresponsive PEGylated ferrocene derivatives (FcPEG) and ferrocene containing surfactants (FcTMA). Using 'smart' thermoresponsive cocatalyst at low concentrations, rate enhancements in BMA and BzMA polymerizations are observed, with good catalyst removability. Using the FcTMA cocatalyst surfactant, increasing

monomer hydrophobicity is shown to increase the polymerization rate and initiator efficiency.



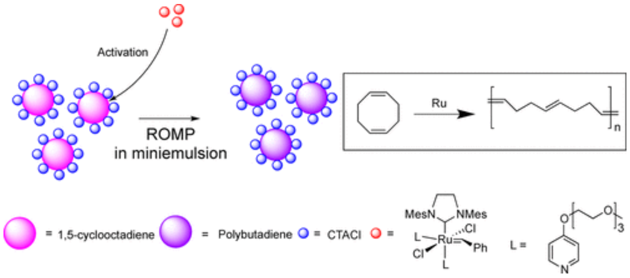
Olga Lidia Torres-Rocha, Xiaowei Wu, Chunyang Zhu, Karen Moffat, Cathleen M. Crudden, and Michael F. Cunningham. "Polymerization-induced self-assembly (PISA) of 1,5-cyclooctadiene using ring opening metathesis polymerization (ROMP)" Macromolecular Rapid Communications (2019), 40, 1800326.

Abstract: Ring opening metathesis polymerization (ROMP) is a technique that allows the synthesis of well-defined linear polyolefins. Polymerization–induced self-assembly (PISA) involves the synthesis of amphiphilic block copolymers: a hydrophilic block is first polymerized homogeneously in solution (usually water) followed by polymerization of a second hydrophobic block, resulting in a diblock copolymer that self-assembles. In this communication, we present preliminary results of the development of PISA for the synthesis of amphiphilic block linear polyolefins via ROMP using a water-soluble PEGylated ruthenium alkylidene catalyst. In the first step, a water-soluble modified-norbornene monomer was polymerized in water, then 1,5-cyclooctadiene (COD) was added to the system to produce amphiphilic block polyolefins. By varying the concentrations of hydrophilic versus hydrophobic monomer, stable latexes with final particles of ~200 nm diameter were prepared.

Zhu, Chunyang; Wu, Xiaowei; Zenkina, Olena; Zamora, Matthew T.; Moffat, Karen; Crudden, Cathleen M.; Cunningham, Michael F. Ring opening metathesis polymerization in miniemulsion using a TEGylated ruthenium-based metathesis catalyst, Macromolecules (2018), 51, 9088-9096.

Abstract: Ring opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD) in miniemulsion was conducted utilizing a water soluble TEGylated ruthenium alkylidene catalyst that was designed to undergo phase transfer from the aqueous phase to the monomer droplets or polymer particles following activation. The catalyst yielded colloidally stable latexes with ~100% conversion, often in less than one hour. Kinetic studies revealed first-order kinetics with good livingness as confirmed by the shift of gel permeation chromatography (GPC) traces. Depending on the surfactants used, the particle

sizes ranged from 100 to 300 nm with monomodal distributions. The more strained cyclic olefin norbornene (NB) could also be efficiently polymerized in miniemulsion with full conversion and without coagulum formation.

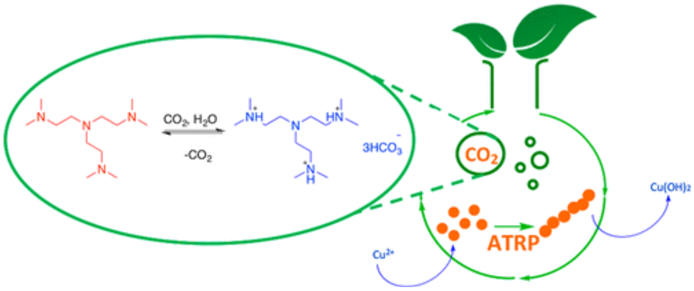


Cummings, Shidan; Trevino, Esther; Zhang, Yujie; Cunningham, Michael; Dubé, Marc A.. Incorporation of Modified Regenerated Starch Nanoparticles in Emulsion Polymer Latexes, Starch (2018), https://doi.org/10.1002/star.201800192

Abstract: Emulsion polymerization produces a water-borne latex (without the use of solvents), and requires low catalyst concentrations to proceed, making it a more sustainable way to produce polymers than many alternatives. The addition of bio-sourced materials to the formulation further increases sustainability. Vinyl functionalized regenerated starch nanoparticles (RSNPs) are used in semi-batch emulsion polymerizations to prepare starch-incorporated latexes with reduced synthetic polymer content. Nanoparticles with 3 wt% concentration of a polymerizable functionalized sugar-based monomer (FSM) of medium hydrophobicity are incorporated with the polymer particles. Latexes with 15 wt% RSNP loading (dry RSNP/total solids) and 40 wt% total solids achieved an RSNP incorporation with the latex particles of up to 10 wt% of the total RSNPs added to the emulsion formulation, or 1.5 wt% of total solids. A modified RSNP feed strategy at higher loadings of 40 and 50 wt% results in 10 wt% incorporation of the total RSNPs, or 4 and 5 wt% of total solids, respectively. With RSNPs produced using a higher concentration of FSM (6 wt%), 20 wt% RSNP incorporation with the latex particles (8 wt% of total solids) is achieved at 40 wt% RSNP loading. Strategies are successfully developed to incorporate a certain amount of the RSNPs with the synthetic polymer particles at high overall RSNP loadings.

Su, Xin; Jessop, Philip G.; Cunningham, Michael F.. ATRP Catalyst Removal and Ligand Recycling Using CO_2-Switchable Materials, Macromolecules (2018), 51, 8156-8164.

Abstract: We have designed three approaches to remove copper catalyst and recycle the ligands after atom transfer radical polymerizations, all based on using materials whose properties can be switched using only CO2 and any nonacidic gas (e.g., air, nitrogen, and argon) as triggers. The first approach involves use of a CO2-switchable solvent (Cy2NMe, N,N-dicyclohexylmethylamine) as the medium for the ATRP reaction. After addition of water to the polymerized reaction mixture and sparging with CO2, the polymer precipitates while the copper salt remains in the solvent. The second approach involves using a conventional ATRP solvent such as toluene to conduct the polymerization. Following polymerization, addition of water and CO2 sparging result in the ligand (Me6TREN) and copper salt transferring into the aqueous phase, while the polymer remains in the organic phase. Finally we demonstrate the effectiveness of the approach in ARGET ATRP using less ligand and copper salt. Residual copper in the polymer was <30 ppb using the switchable solvent and <15 ppb in toluene, while residual nitrogen was <90 ppm using the switchable solvent and <35 ppb in toluene. The feasibility of recovering and reusing the ligand for subsequent polymerizations is also established.



A. Darabi, A.R. Shirin-Abadi, S. Avar, P.G. Jessop, M.F. Cunningham. Surfactant-Free Emulsion Copolymerization of Styrene and Methyl Methacrylate for Preparation of Water-Redispersible Polymeric Powders, Journal of Polymer Science Part A: Polymer Chemistry (2018), 56, 2376–2381.

Abstract: Poly(methyl methacrylate), polystyrene, and poly(styrene-*co*-methyl methacrylate) cationically stabilized latexes with up to 25% solid content were prepared by surfactant-free emulsion polymerization (SFEP) employing 1 mol % 2,2′-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as an initiator and stabilizer (inisurf) with respect to monomer at 70 °C. The latexes had 200–500 nm *z*-diameter and a very narrow size distribution (PDI < 0.05). The stabilizing amidinium moieties from VA-044 were covalently bound to the particles. After drying in air, poly(styrene-*co*-methyl methacrylate), PS-*co*-PMMA latexes were easily redispersible in water simply by addition of water and a few minutes of gentle stirring. The redispersed latex particles had colloidal characteristics very similar to the original latex particles in terms of polydispersity, size, and zeta potential. In contrast, latexes prepared with a similar formulation but using a conventional cationic surfactant (CTAB) that was not covalently bound to the particles were not redispersible. This is the simplest method reported so far for the preparation of redispersible latexes that do not use high stabilizer concentrations.

J. Glasing, P.G. Jessop, P. Champagne, M.F. Cunningham. Graft-modified cellulose nanocrystals as CO_2-switchable Pickering emulsifiers, Polymer Chemistry (2018), 9, 3864-3872.

Abstract: We report the use of a bio-sourced Pickering emulsifier based on cellulose nanocrystals (CNCs) grafted with less than 25 wt% of synthetic, CO_2-responsive polymer for the reversible emulsification/demulsification of oil and water. CO_2-responsive CNCs were previously prepared by grafting poly(*N*-3-(dimethylamino) propyl methacrylamide)

(PDMAPMAm) and poly(*N*,*N*-(diethylamino)ethyl methacrylate) (PDEAEMA) to the CNC surface using nitroxide-mediated polymerisation (NMP) in water as a benign solvent. The surface and interfacial properties of the graft-modified CNC were characterised by surface and interfacial tensiometer measurements, and the resulting droplets obtained from emulsions were visualised using optical microscopy. The emulsification/demulsification process was found to be responsive to N_2 and CO_2, reversible and easily repeatable. The Pickering emulsifiers could be recovered after application, which would make this technology particularly interesting for oil–water separation and enhanced oil recovery. The pK_{aH} of the grafted polymer and the polarity were correlated to the CO_2 sparging time required to break the emulsion and to the emulsion stability (lifetime). The effects of the chain length of the grafted polymer, graft densities, total amount of CO_2-switchable groups on the CNC surface, and concentration of Pickering stabiliser on the properties of emulsions were investigated.

A.R. Shirin-Abadi, M. Gorji, S. Rezaee, P.G. Jessop, M.F. Cunningham. CO2-switchable-hydrophilicity membrane (CO2-SHM) triggered by electric potential: faster switching time along with efficient oil/water separation, Chemical Communications (2018), 54, 8478-8481.

Abstract: We report a membrane that can be reversibly switched between a hydrophilic state and a hydrophobic state simply by alternately bubbling CO_2 into and passing electric potential (EP) through a solution in contact with the membrane. The prepared membrane could be effectively used for oil/water separation.

Z. Yujie, M. F. Cunningham, N. M. B Smeets, M. A. Dube. Starch nanoparticle incorporation in latex-based adhesives, European Polymer Journal (2018), 106, 128-138.

Abstract: Starch nanoparticles (SNPs) are chosen as renewable alternatives to partially replace petroleum-based monomers and produce bio-based latexes for adhesive applications. To maintain adhesive performance, SNPs are modified (i.e., via increasing cross-link density, vinyl functionalization, and adjusting hydrophilic/hydrophobic balance) to facilitate their incorporation into the latex particles. The modified SNPs are then polymerized in a semi-batch emulsion polymerization at 60 °C, and yield low viscosity latexes with up to 17 wt% SNP loading and 42 wt% solids. TEM/STEM imaging is performed and reveals the presence of a core-shell particle morphology. This is supported by comparing the adhesive properties of SNP-containing latex films from an *in situ* preparation vs. a blend of acrylic latex with SNPs. The results suggest that the modified SNPs were largely encapsulated into the latex particles rather than in the aqueous phase or at the latex particle/water interface.

S. Cummings, M. F. Cunningham, M. A. Dube. The use of amylose-rich starch nanoparticles in emulsion polymerization, Journal of Applied Polymer Science (2018), 135 (28), 46485.

Abstract: Regenerated starch nanoparticles (RSNPs) produced from dent corn, an amylose-rich source of starch, are added to an emulsion polymerization. To reduce or eliminate the challenges of polymerizing in the presence of amylose-rich starch, a seeded, semibatch, monomer-starved approach is used. To prevent the accumulation of water soluble amylose in the aqueous phase, reaction with a hydrophobic compatibilizing monomer, butyl acrylate, is used prior to the primary butyl acrylate/methyl methacrylate/acrylic acid feed. In addition, an elevated initiator concentration is used in the seed stage to reduce the molecular weight of the soluble starch and promote grafting. The procedure yields a 100.0 cp latex with 40 wt % solids, 25 wt % RSNP loading, and 40 wt % incorporation.